THE SYNTHESIS and STUDY

of

POLYCYCLIC AROMATIC HYDROCARBONS.

T H E S I S

presented by

Alexander McCallum, B.Sc. (Glasgow)

for the Degree of

DOCTOR OF PHILOSOPHY

of the

University of Glasgow.

May, 1963.

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S U M M A R Y

of a Thesis entitled

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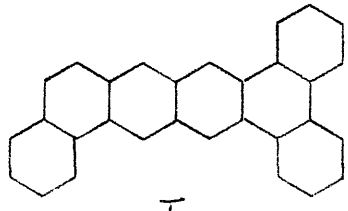
1.2-3.4-7.8-Tribenzotetracene (I) was prepared to demonstrate the importance of benzenoid rings in the stabilisation of aromatic hydrocarbons. Examination of the series of isomeric hydrocarbons having seven rings, indicates that stability increases with the number of benzenoid rings.



I

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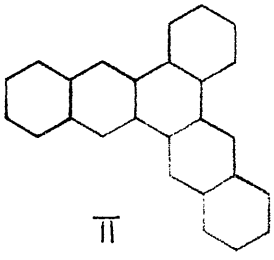

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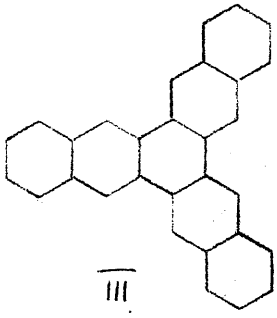

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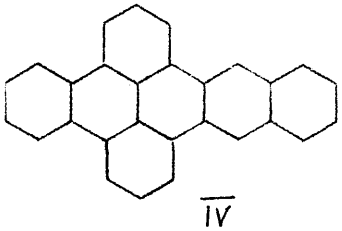
Two previously unknown linear pyrenes, 1.2-benzo-naphtho-[2",3"-7.8]-pyrene (IV) and 1.2-benzo-anthraceno-[2",3"-7.8]-pyrene (V) were synthesised and the ideas in the last paragraph were found to be fully applicable to these.



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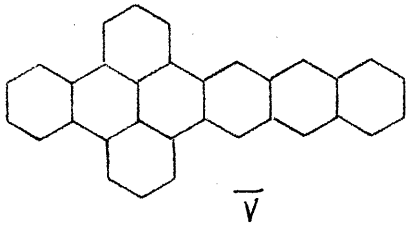

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The fully benzenoid hydrocarbon, 1.12-2.3-6.7-8.9-tetrabenzanthanthrene (VI) was prepared. This exhibits all the characteristics of these extremely stable compounds. Thus it is insoluble in concentrated sulphuric

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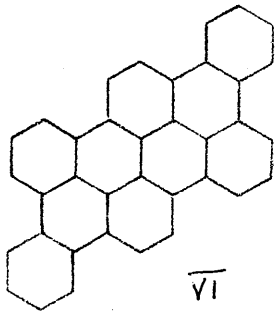

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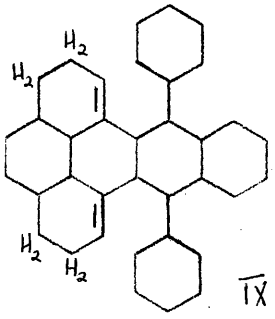
The two hitherto unknown hydrocarbons, 1.2-3.4-5.6-tribenzocoronene (VII) and 1.12-o-phenylene- 2.3-10.11 - dibenzoperylene (VIII) were made. These proved to be sterically strained. In the course of these syntheses, two quino-dimethides (IX) and (X) were obtained. These are both quite stable.



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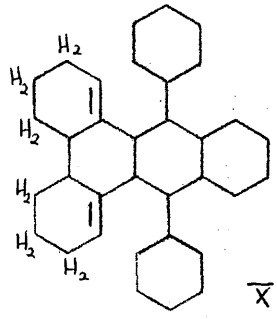

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Various attempts to prepare 1.2-5.6-9.10-tribenzo-coronene are recorded. None of these was successful, but a material which is thought to be a mixture of 7.8-benzo-

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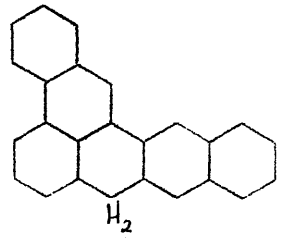

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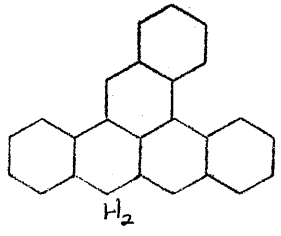

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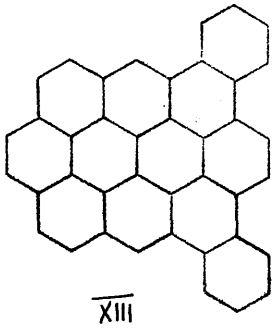

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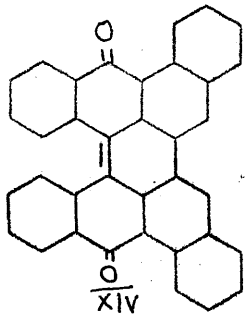

XIV

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ACKNOWLEDGEMENTS.

I am delighted to have this opportunity to express my appreciation to Dr. E. Clar for his assistance and inspiration throughout the course of this work.

I would like to thank the Department of Scientific and Industrial Research for a subsistence allowance during the period of my study, and also to thank Mr. J.M. Cameron and his staff who executed the micro-analyses contained herein.

Mr. R.A. Robertson was associated with me in the work outlined in Chapter II of this Thesis and I gratefully acknowledge his industry.

PUBLICATIONS.

The following papers have been or are about to be published:

(1) The Significance of Benzenoid Rings for the Stability of Aromatic Hydrocarbons.

E. Clar and A. McCallum.
Tetrahedron, 10, 171, (1960).

(2) Asymmetric Annellation Effects - VI.

E. Clar, A. McCallum and R.A. Robertson.
Tetrahedron, 18, 1471, (1962).

(3) 1.12-2.3-6.7-8.9-Tetrabenzanthanthrene.

E. Clar and A. McCallum.
Tetrahedron, in press.

(4) Annellation Effects in the Pyrene Series and Classification of Absorption Spectra.

E. Clar, J.F. Guye-Vuilleme, A. McCallum and I.A. Macpherson.
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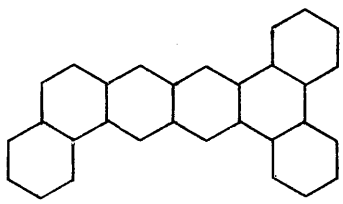

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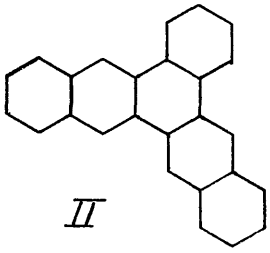

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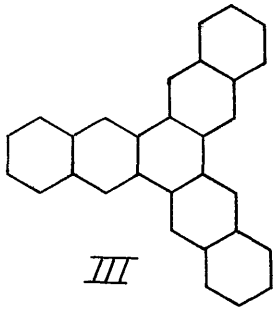

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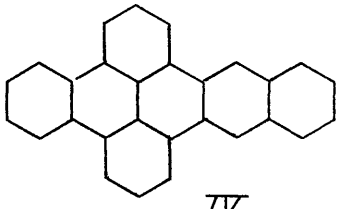

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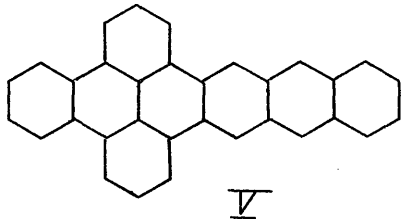

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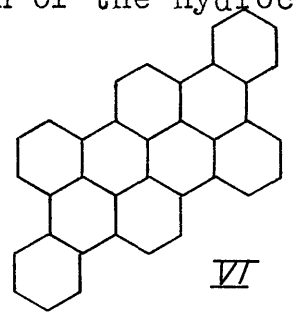

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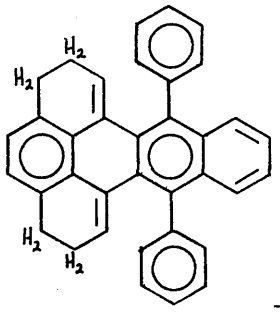

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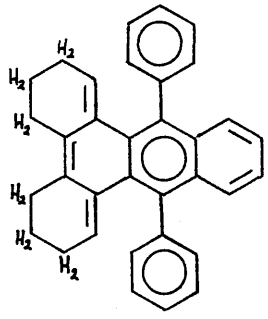

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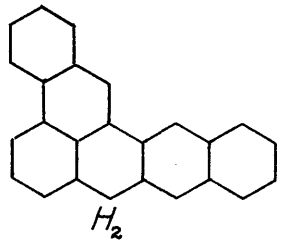

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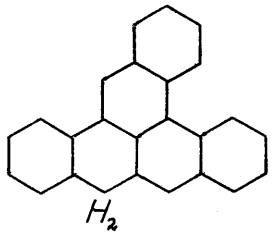

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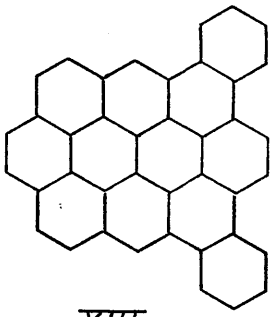

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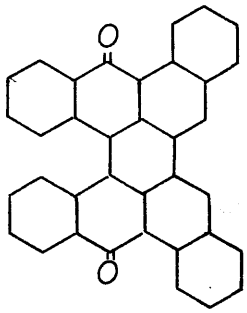

XIV

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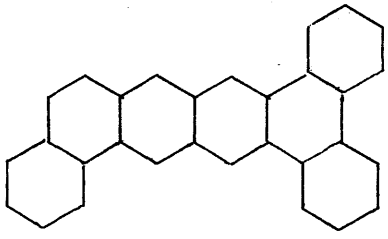
C H A P T E R I.

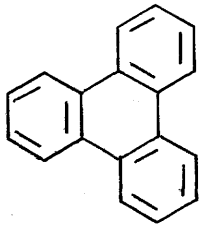
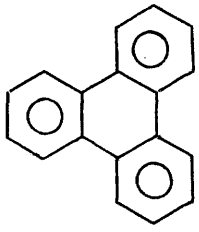
1.2-3.4-7.8-TRIBENZOTETRACENE.[1]



I

INTRODUCTION: The previously unknown hydrocarbon, tribenzotetracene (I), was prepared in order to demonstrate the importance of the benzenoid ring for the stabilisation of aromatic hydrocarbons. In addition, further confirmation of CLAR'S general rule[2] that annellation to already fixed double bonds produces only small shifts in β-band wavelengths was provided by the absorption spectrum of the hydrocarbon.

THEORETICAL DISCUSSION: A benzenoid ring in a polycyclic aromatic hydrocarbon may be simply defined as a ring which possesses three conjugated double bonds, i.e. three pairs of π-electrons in an aromatic sextet.[3] The convention, introduced by Sir Robert ROBINSON,[4] of representing these aromatic sextets by circles will be used throughout this work. It is then obvious that triphenylene (II) contains three benzenoid rings and may be written -

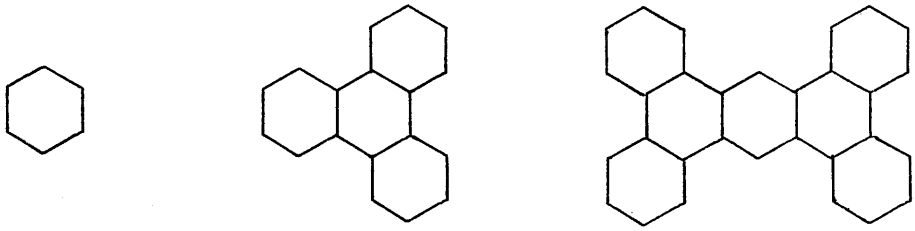
 or better 

II

These are known as inherent benzenoid rings since each set of six π-electrons is possessed exclusively by one ring.

A brief digression will now be necessary for consideration of the electronic structure of the benzenoid ring. If two diphenyl units are success-

ively annellated to benzene, the following series is obtained:



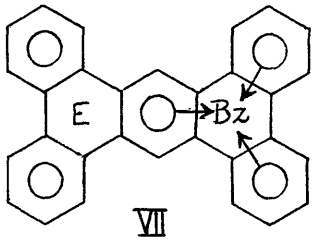
λ_β = 1819 $\xrightarrow{+751}$ 2570 $\xrightarrow{+355}$ 2925 $\mathring{A}$

$\sqrt{\lambda_\beta}$ = 42.65 $\xrightarrow{+8.05}$ 50.70 $\xrightarrow{+3.40}$ 54.10 $\sqrt{\mathring{A}}$

The above shifts are preferably recorded in $\sqrt{\mathring{A}}$ which is a scale for reciprocal nuclear charges.(5)

The second shift is unexpectedly small and constitutes an asymmetric annellation. The phenomenon is explained by subtracting the second shift ($3.40\sqrt{\mathring{A}}$) from the β-band of triphenylene ($50.70\sqrt{\mathring{A}}$). The result is a β-band at $47.30\sqrt{\mathring{A}}$ or $2237\mathring{A}$ which is practically identical with the wavelength of the β-band of naphthalene ($2210\mathring{A}$ in alcoholic solution). Thus the conjugation of the central unit of tetrabenzanthracene is equivalent to that of naphthalene and hence one of the central rings must be incapable of contributing to conjugation. This indicates that one ring (E) of the central unit possesses no elect-

rons while the other has, by virtue of the transfer of π-electrons from adjacent rings, attained aromaticity. It must therefore be concluded that each inherent benzenoid ring can transfer only two π-electrons to adjacent rings. Thus in tetrabenzanthracene (VII)



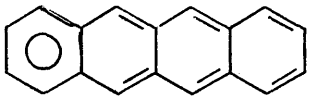
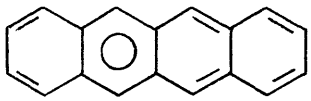
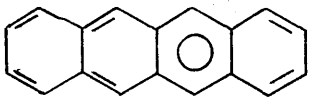
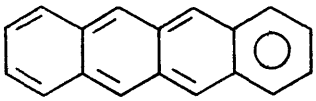
VII

there must be a new benzenoid ring formed by donation of two π-electrons from each of the neighbouring inherent sextets. This new ring is termed an induced benzenoid ring (Bz).[5] [6]

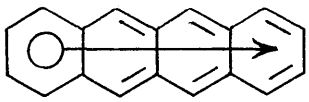
This line of reasoning indicates that of the six π-electrons in a benzenoid ring, two are at a higher electronic level than the others, and are capable of migration, while the remaining four -electrons are confined to the ring. The HÜCKEL Term Scheme[7] also predicts two electronic levels but here the lower level is occupied by two, and the next higher by four π-electrons.

It is apparent that an acene can have only one benzenoid ring, the other rings of the system being o-quinonoid. However, two π-electrons from the

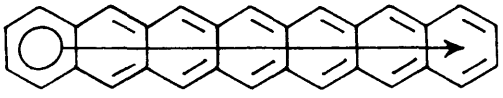
sextet may migrate through the system and hence confer a fractional aromatic character to each individual ring of the molecule. In tetracene, for example, four possibilities arise:-

This may be more conveniently written with an arrow to symbolise the movement of the two delocalised π-electrons. Thus -

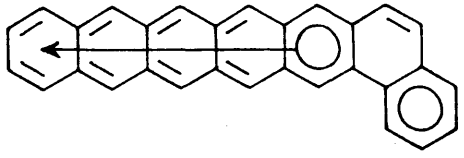


This treatment of acenes accounts well for the observed gradations in reactivity, spectra, color, stability, etc. from the very stable benzene to the extremely reactive heptacene which has its aromatic sextet distributed over seven rings. Obviously an acene with an infinite number of rings would possess no aromatic character but would be merely a cyclic



dark green

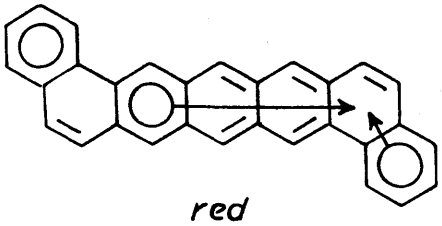
III



blue-green

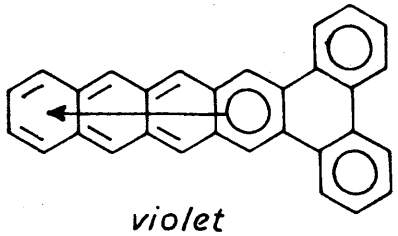
IV

λ_p = 6510 —1280→



red

V

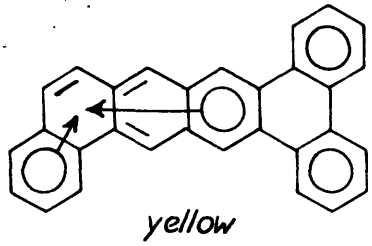


violet

VI

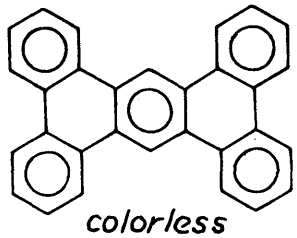
λ_p = 5230 +155→ 5385 —1155→

λ_β = 3470 —40→ 3430 —150→



yellow

I



colorless

VII

λ_α = --- → ---

λ_p = 4230 —895→ 3335 Å

λ_β = 3280 —330→ 2950 Å

FIGURE 1.

Comparison of Isomeric Hydrocarbons with Seven Rings.

polyene. Thus benzenoid rings serve to stabilise the acenes, and it is of interest to enquire if this is a general occurrence. That it is may best be shown by a consideration of isomeric hydrocarbons all having seven rings. (see Figure 1).

Heptacene (III), having seven linearly annellated rings is dark green and so reactive that it has not yet been obtained in a pure state.[8] The angular arrangement of a ring adds an extra sextet in 1.2-benzohexacene (IV),[9] which is blue-green and obtainable in a pure state. Correspondingly, the angular annellation of further rings enhances the stability of the system and hence we come to the red 1.2-8.9-dibenzopentacene (V), and the violet-red 1.2-3.4-dibenzopentacene (VI).[10] These hydrocarbons differ little spectrally, but both are very different from (IV), and there is a large shift to the violet from the spectrum of (IV) to those of (V) or (VI). Further large violet shifts are observed in the transition to the yellow. 1.2,3.4,7.8-tribenzotetracene (I)[1] which reacts more slowly with maleic anhydride than most benzotetracenes. A smaller violet shift is observed in the final annellation to 1.2,3.4,5.6,7.8-tetrabenzoanthracene (VII). This latter is a color-

less compound which is extremely stable.[11]

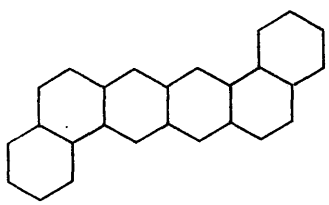
Examination of this series of hydrocarbons shows clearly that the properties of the constituent members are dependent upon the number of benzenoid rings possessed by each molecule.

Since benzenoid rings obviously enhance the stability of hydrocarbons, it is evident that systems containing only benzenoid rings must be unusually stable. These are known as fully benzenoid hydrocarbons or alternately as condensed polyphenyls, and they will be more fully discussed in Chapter IV.

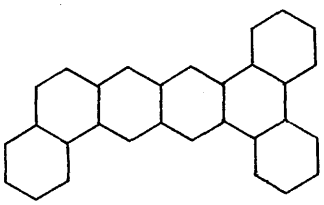
Attempts have recently been made to extend HÜCKEL'S[12] rule to polycyclic hydrocarbons. The rule states that aromatic stability is conferred on cyclic systems which possess $(2 + 4n)$ π-electrons, n being an integer.[13] Application of this to the acene series indicates that there would be no differentiation between the stable benzene with $(2 + 4)$ π-electrons and the very reactive heptacene with $(2 + 28)$ π-electrons. Even the higher members of the acene series - which are so unstable as to be incapable of isolation - would appear to have a stability commensurate with that of benzene. In addition, the very stable fully benzenoid hydrocarbons have $6n$ π-elect-

rons and in consequence, half of these cannot be accommodated by the rule. Thus it is obvious that HÜCKEL'S rule is not applicable to polycyclic hydrocarbons.

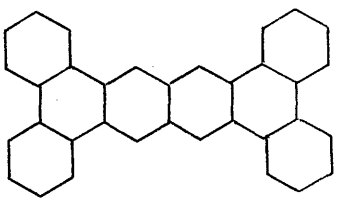
In the annellation series, dibenzotetracene (VIII), tribenzotetracene (I) and tetrabenzotetracene (IX) only small shifts of the β-bands occur:



VIII



I

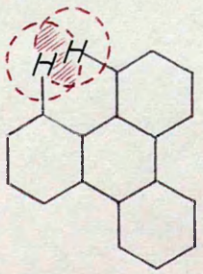


IX

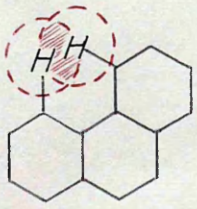
λ_α=	--		--		4140	Å
λ_p=	4375	-125 →	4250	-350 →	3900	Å
λ_β=	3255	+25 →	3280	0 →	3280	Å

This effect may be explained if dibenzotetracene (14) is given the maximum number of benzenoid rings. Then the two terminal double bonds in the central tetracene unit appear to be fixed, and experience has shown that annellation to fixed double bonds produces only small shifts of β-bands. Further examples of this phenomenon are numerous, and will be dealt with in later Chapters of this work.

EXPERIMENTAL DISCUSSION: Numerous Friedel-Crafts reactions have been conducted with triphenylene (II) and it has been found that reaction occurs exclusively at the 2-positions, no instance being recorded of attack at the 1-positions.[15] This lack of reactivity of the 1-positions is probably due to the sterically overcrowded hydrogen atoms at these points which hinder the approach of attacking entities. This same resistance to attack may also be observed in the 4-positions of phenanthrene (X) where the environment is the same.



II



X

In accord with this, 2-methyl-1-naphthoyl-2'-triphenylene ketone (XI) was prepared in good yield by the reaction of 2-methyl-1-naphthoyl chloride[16] with triphenylene in the presence of aluminium chloride. This ketone was then pyrolised at 400-420° under the protection of carbon dioxide. Sublimation of the dark residue obtained yielded a yellow material which on

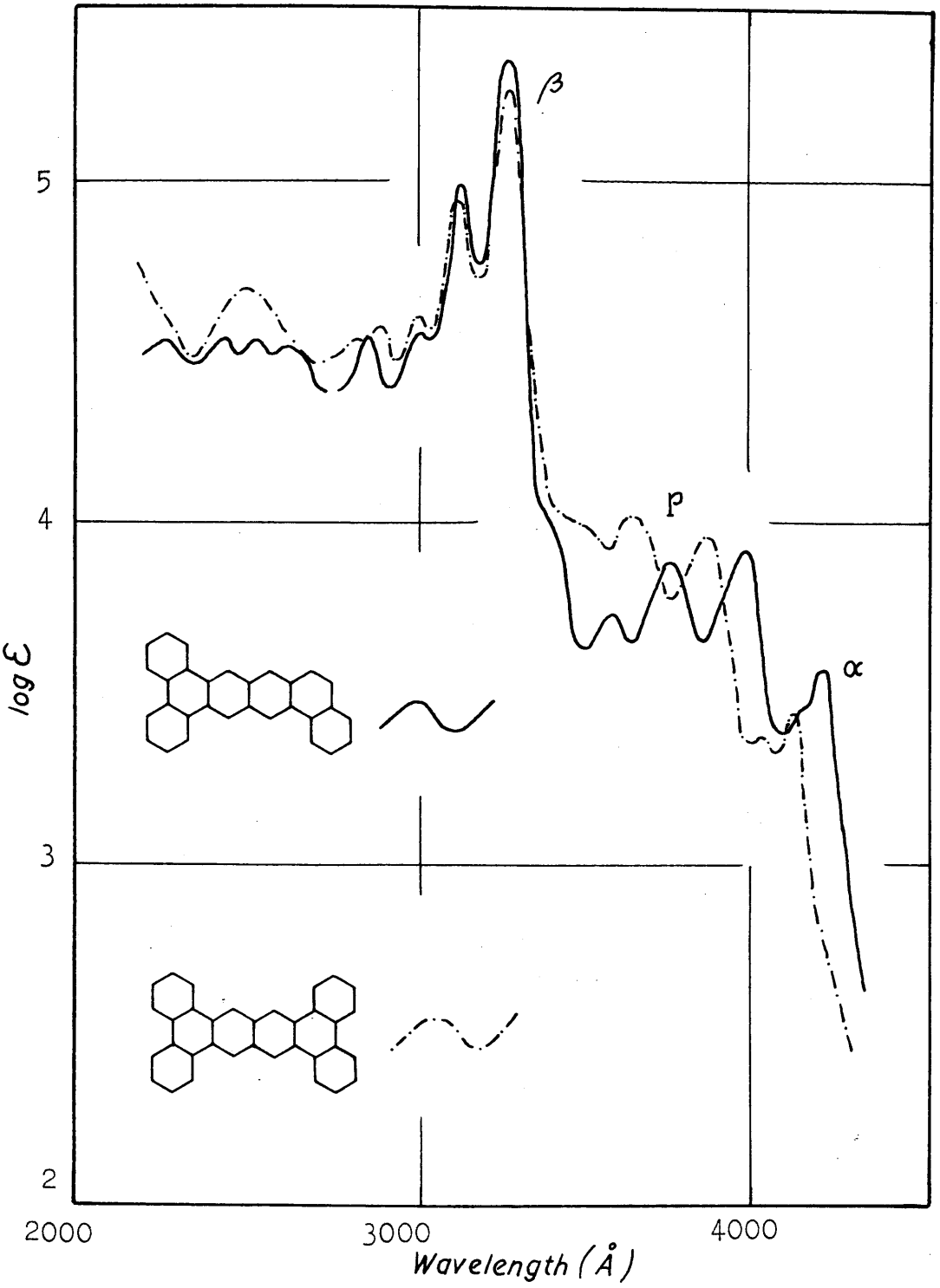
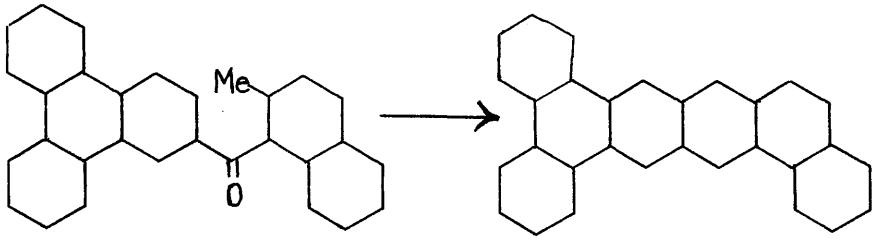


FIGURE 2. Absorption max.(A) and log (in parentheses). 1.2-3.4-7.8-Tribenzotetracene (I) in benzene, α:4230 (3.56); p:4000 (3.92), 3780 (3.89), 3590 (3.73); β:3280 (5.36), 3130 (4.96), 3020 (4.56); 2870 (4.55); in cyclohexane, 2630 (4.50), 2530 (4.52), 2430 (4.52), 2270 (4.53). 1.2-3.4-7.8-9.10-Tetrabenzotetracene in benzene, α:4140 (3.50); p:3900 (3.98), 3680 (4.06); β:3280 (5.30), 3140 (4.90), 3010 (4.60), 2900 (4.58); in heptane, 2530 (4.68).

crystallisation from xylene proved to be non-uniform. Further purification consisted of forming the



XI I

tribenzotetracene adduct with maleic anhydride and extracting this from the mixture with dilute alkali, when a white insoluble material remained. Acidification of the alkali solutions gave the white adduct which sublimed from soda-lime as yellow needles of tribenzotetracene (I). This crystallised from xylene in two forms - on slow cooling of the solution, long yellow needles, but on faster cooling, small yellow balls. These had identical melting points and spectra. The spectrum of 1.2-3.4-7.8-tribenzotetracene is given in Figure 2.

Tribenzotetracene-maleic anhydride adduct (XII) was obtained by refluxing the pure hydrocarbon with maleic anhydride. The absorption spectrum of the disodium salt of this adduct is given in Figure 3. It

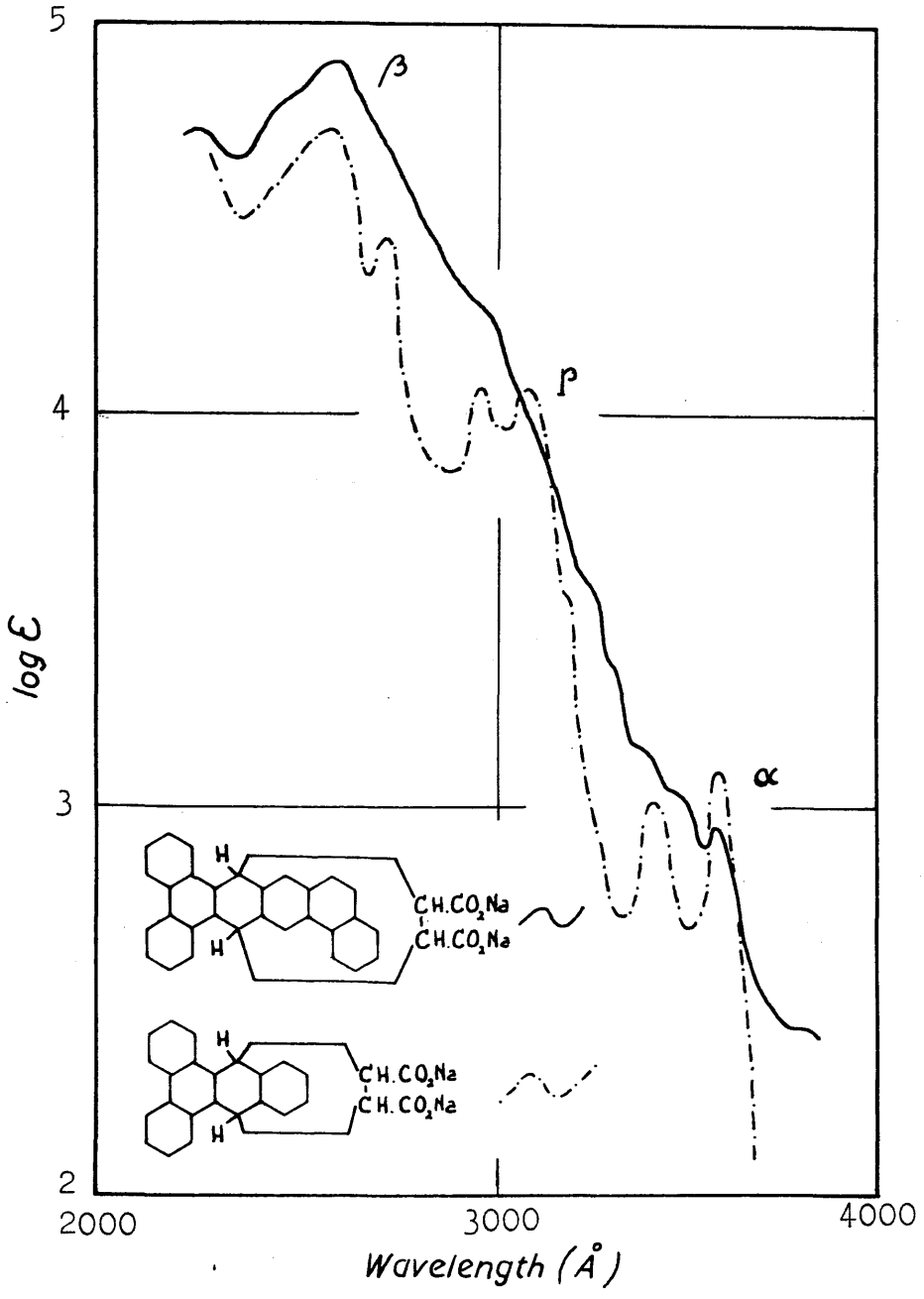
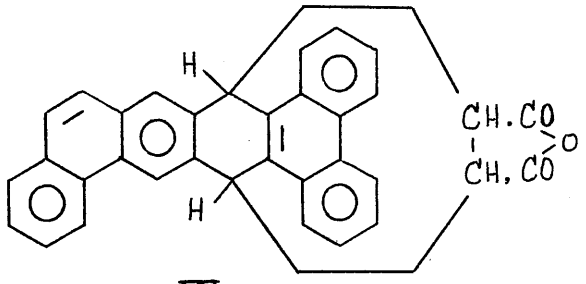


FIGURE 3. Absorption max. (Å) and log (in parenthesis). Disodium salt derived from (XII) in water, p:3580 (2.92); β:2610 (4.89). Disodium salt of the adduct of 1.2-3.4-dibenzanthracene and maleic anhydride. (E. Clar, Ber. Dtsch. Chem. Ges. 65, 507 (1932) in water, α:3590 (3.08), 3420 (2.98); p:3100 (4.06), 2980 (4.05), 2740 (4.44); β:2600 (4.70).

is consistent with the spectrum of a 9.10-disubstituted phenanthrene and hence addition of maleic



XII

anhydride to tribenzotetracene must take place in the 5.12-positions.

-------oOo-------

EXPERIMENTAL.

2-METHYL-1-NAPHTHOYL-2'-TRIPHENYLENYL-KETONE (XI).

To triphenylene (7g) and 2-methyl-1-naphthoyl chloride[16] (7g) in chlorobenzene (20ml) or in benzene (50ml) powdered aluminium chloride (12g) was added. After slight warming the reaction began and the triphenylene went into solution. The dark reddish-yellow mixtute was heated to 50° for a few minutes until the evolution of hydrogen chloride ceased. After decomposition with dilute hydrochloric acid, the solvent was removed by steam distillation. The resinous residue crystallised when treated with ether. The ketone (XI) was recrystallised first from xylene and then from acetic acid. It formed very pale yellow needles, m.p. 214-216°, which dissolved in concentrated sulphuric acid to form a red solution.

Found: C, 90.6 ; H, 4.9

$C_{30}H_{20}O$ requires: C, 90.9 ; H, 5.1%

1.2-3.4-7.8-TRIBENZOTETRACENE (I).

The ketone (10g) was heated to 400-420° under the protection of a current of carbon dioxide. The formation of water was completed after ½ hour. The residue was sublimed at 270°/1mm. Triphenylene (0.77g) was first obtained, followed by the yellow hydrocarbon at 350°/1mm. The crude hydrocarbon was recrystallised from xylene and was found to be non-uniform (1,97g). For further purification it was transformed into the adduct (XII) with boiling maleic anhydride. The excess of maleic anhydride with boiling water and the residue several times extracted with sodium hydroxide in aqueous alcoholic solution. This left a colorless by-product undissolved which was filtered off. The united filtrates were acidified with hydrochloric acid and the white precipitate (1.1g) washed with water and dried.

The adduct was mixed with soda lime (1.5g) and sublimed at 300°/o.1mm. The tribenzotetracene which formed yellow needles was repeatedly recrystallised from xylene. When the solution was quickly cooled it yielded yellow wart-like conglomerates, and on slow

crystallisation long needles. The hydrocarbon dissolved in concentrated sulphuric acid with a blue color (absorption band about 6200 Å) which soon changed to green and then to yellow. Both forms have m.p. 277-278°.

Found: C, 95.3 ; H, 4.5

$C_{30}H_{18}$ requires: C, 95.2 ; H, 4.8%

1.2-3.4-7.8-TRIBENZOTETRACENE-MALEIC-ANHYDRIDE ADDUCT (XII).

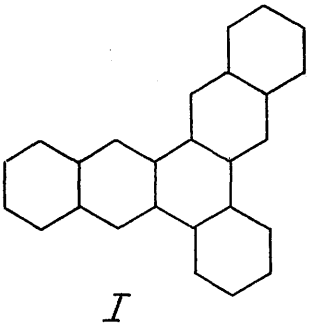
This adduct was obtained by boiling pure tribenzotetracene with excess maleic anhydride. After removing the excess maleic anhydride the adduct was dissolved in aqueous-alcoholic sodium hydroxide filtered and the free acid precipitated with hydrochloric acid. It formed a white powder which decomposed at 190-192°.

Found: C, 82.6 ; H, 4.8

$C_{34}H_{22}O_4$ requires: C, 82.6 ; H, 4.5%

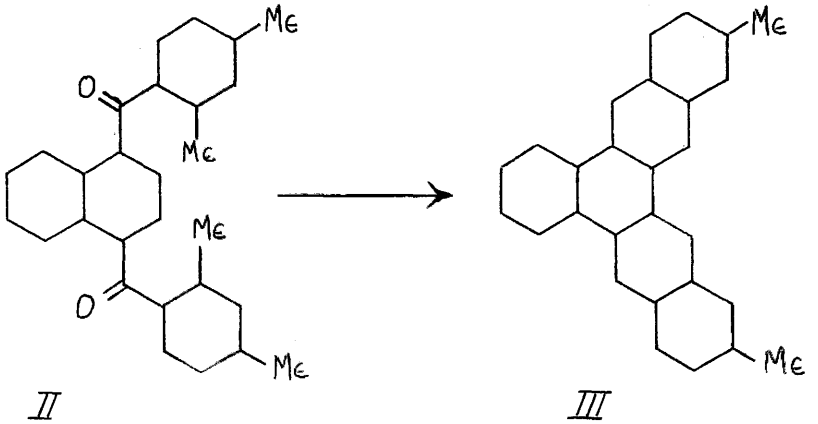
CHAPTER II.

6.7-BENZOPENTAPHENE.[1]



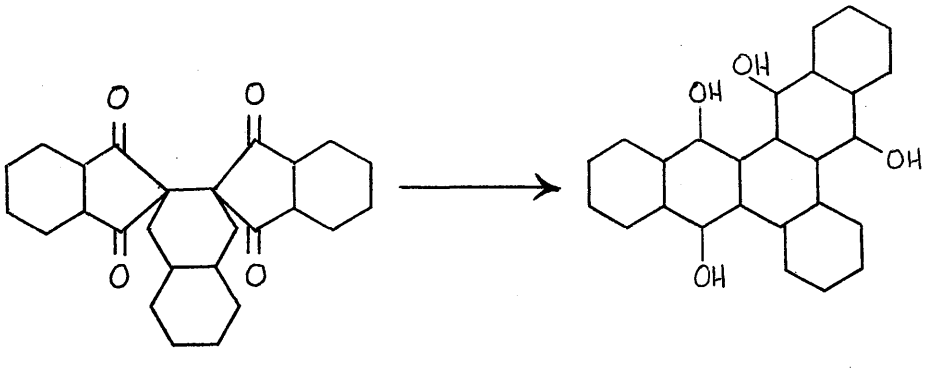
I

INTRODUCTION: The first synthesis of a 6.7-benzopentaphene derivative was recorded in 1925, when 2.11-dimethyl-6.7-benzopentaphene (III) was described in patent.[2] It is probable

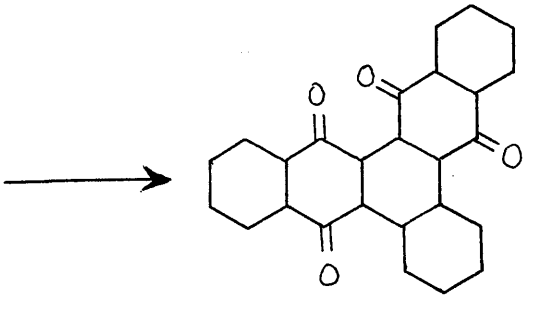


II *III*

that this was obtained by the pyrolysis of 1.4-di-m-xyloylnaphthalene (II). However, rearrangements frequently occur in the pyrolyses of compounds of this type, and the unexpectedly low melting point of the hydrocarbon, 188°, suggests rather that a methyl tetraphene was obtained by fission. 6.7-benzopentaphene diquinone (VI) was prepared by RADULESCU and BARBULESCU[3] by the condensation of o-xylylene bromide with the potassium salt of bisketo-hydrindene and treatment of the resulting compound (IV) with sodium ethoxide. This gave the tetrahydroxy compound (V) which oxidised to the diquinone in the atmosphere.

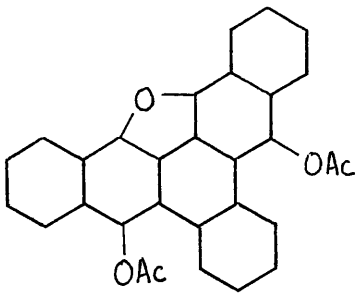


IV V

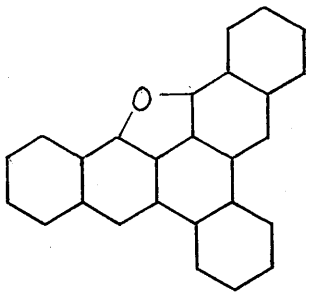


VI

These authors also reported that on reductive acetylation of this diquinone, the diacetyl compound (VII) is formed and on zinc dust distillation the oxy compound (VIII).

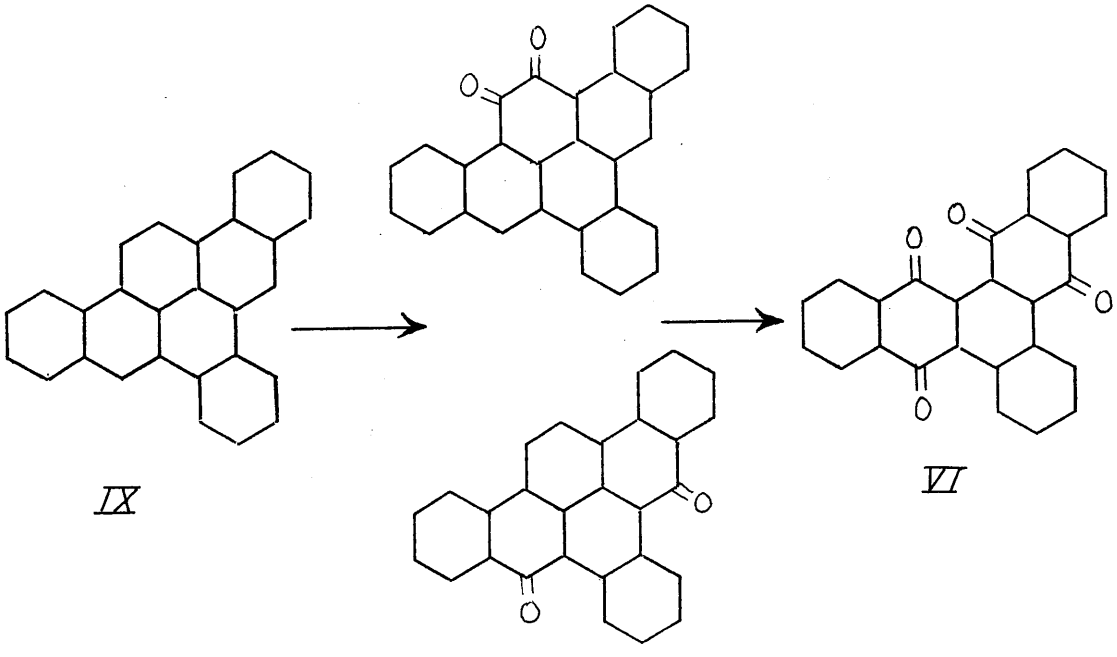


VII



VIII

In a more recent publication, ZINKE and OTT (4) have described a degradative preparation of 6.7-benzopentaphene. The oxidation of 1.2-4.5-8.9-tribenzopyrene (IX) with dichromate and acetic acid gave,



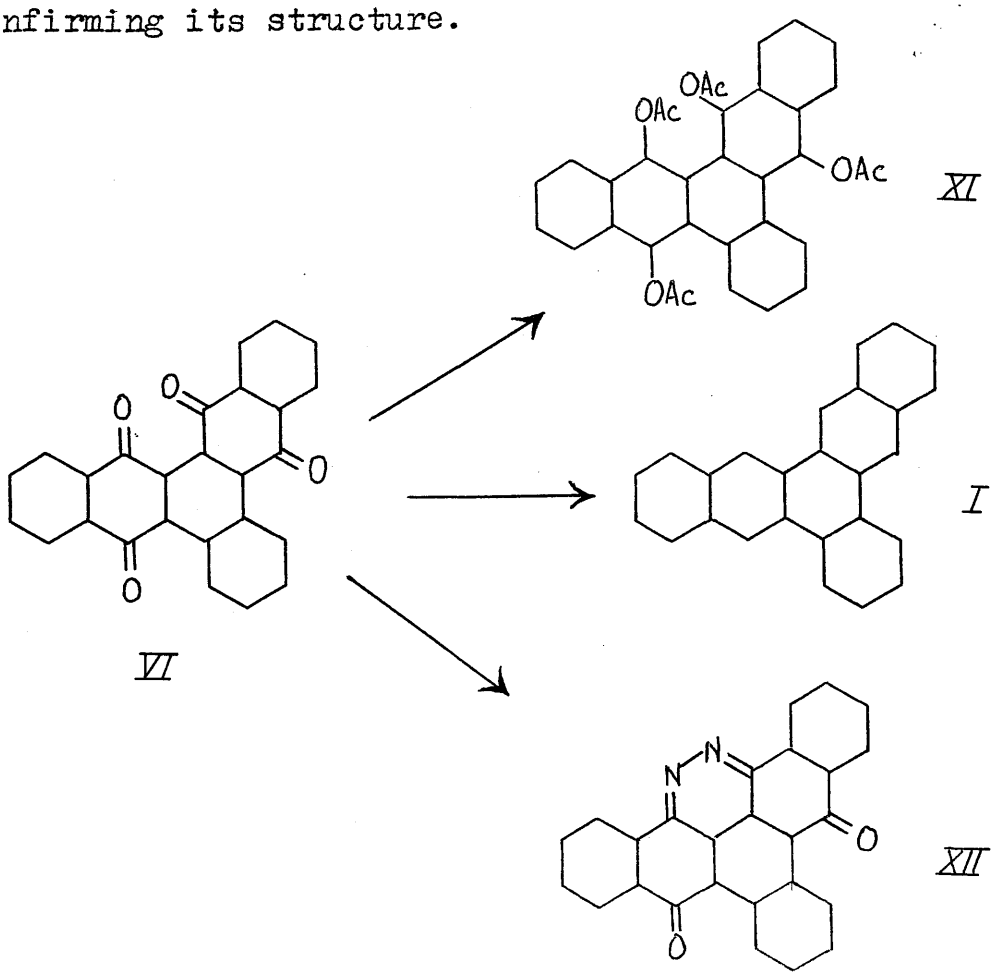
IX

VI

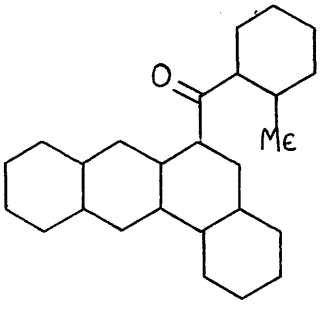
X

along with the expected quinone (X), a small amount of a compound which proved to be identical with the previously mentioned diquinone (VI). This could be obtained as the major product under more drastic conditions.

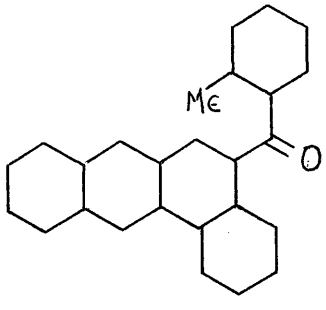
However, contrary to the finding of BARBULESCU and RADULESCU, these authors found that reductive acetylation of this diquinone gave the tetra-acetyl derivative (XI) and that on zinc dust distillation, 6.7-benzopentaphene (I) was obtained. In addition, the diquinone readily formed the azine (XII), thus confirming its structure.



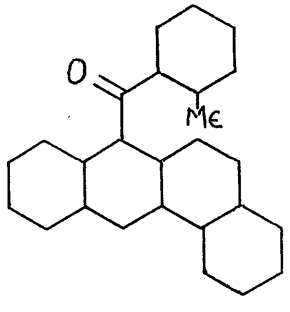
EXPERIMENTAL DISCUSSION: The present work describes a more direct synthetic route to 6.7-benzopentaphene. The reaction of tetraphene with acetic anhydride in the presence of aluminium chloride was found by COOK and HEWETT[5] to give a mixture of five mono-acetyl isomers. However, it was considered likely that a Friedel-Crafts reaction with toloyl chloride, followed by pyrolysis would yield 6.7-benzopentaphene preferentially; also, since the hydrocarbons obtainable from the unwanted keto-isomers would be relatively reactive they would be easily removed by chromatography. Accordingly, this Friedel-Crafts reaction was conducted in methylene chloride solution, and, after decomposition and chromatography, pale yellow needles were obtained. These probably consisted of the isomers (XIIIa), (XIIIb) and perhaps (XIIIc), since after pyrolysis followed by



XIII a



XIII b



XIII c

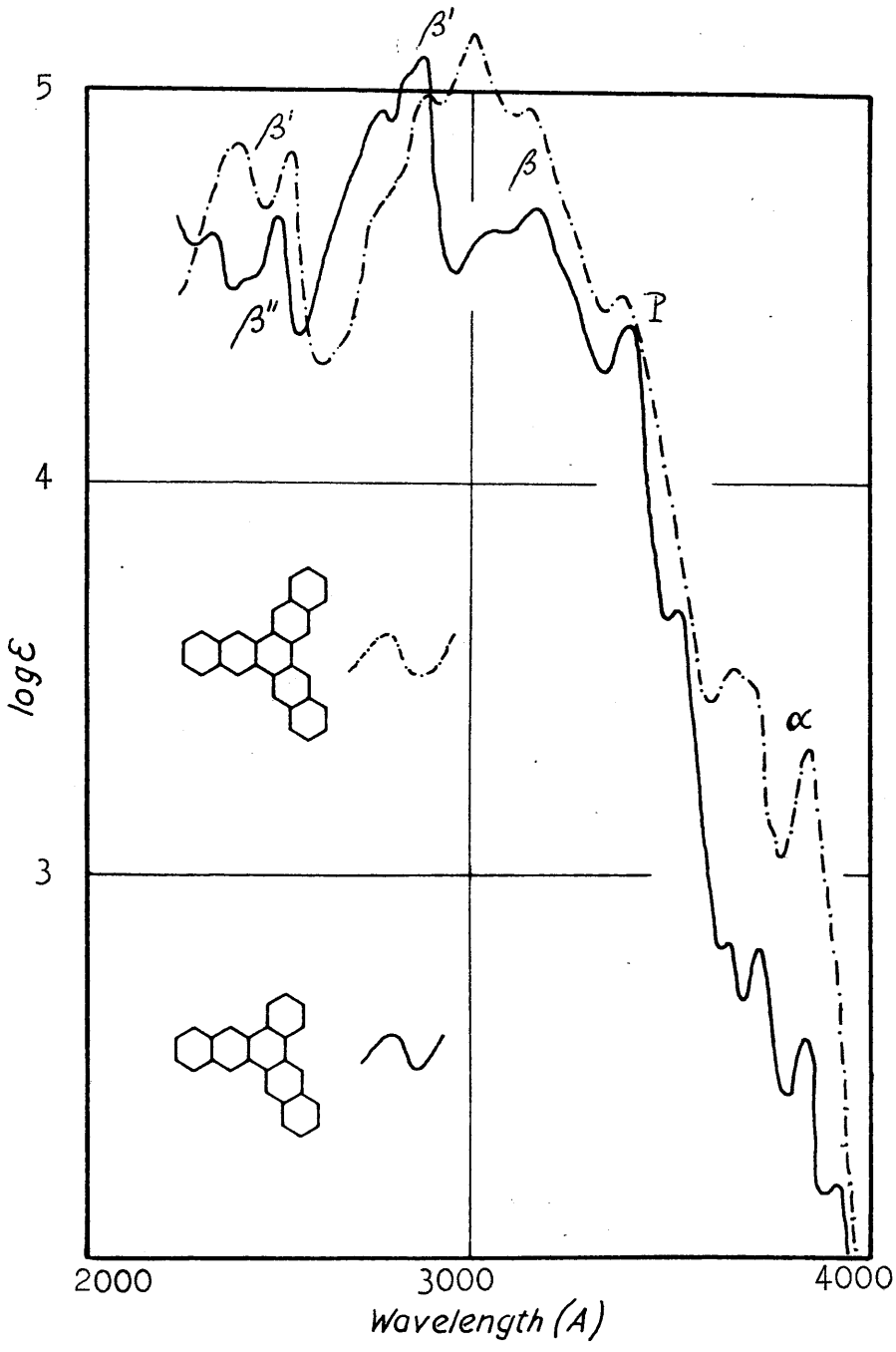
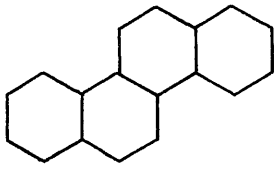


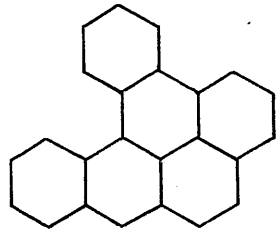
FIGURE 4. Absorption max.(Å) and log (in parenthesis). Naphtho-[2'.3'-6.7]-pentaphene (XXX) in benzene, α :3800 (3.32), 3700 (3.52); p:3400 (4.48); β:3150 (4.96), 3000 (5.15), 2880 (4.99); β':2530 (4.84), 2390 (4.86). From 2800 in cyclohexane. 6.7- Benzopentaphene (I) in cyclohexane, α :3940 (2.20), 3860 (2.58), 3740 (2.80), 3660 (2.81), 3520 (3.66); p:3390 (4.38); β:3140 (4.69), 3040 (4.63), β' :2840 (5.07), 2740 (4.94); β":2460 (4.66), 2300 (4.61).

chromatography, sublimation and repeated crystallisation from xylene, 6.7-benzopentaphene, m.p. 250-251° was obtained. However, since the product described by ZINKE had m.p. 239-240°, our hydrocarbon was oxidised with chromium trioxide in acetic acid and the azine (XII) prepared from the resulting diquinone. Both these compounds proved identical to those obtained by ZINKE. It would therefore appear that the 6.7-benzopentaphene previously described may have contained some of the oxido-compound (VIII) reported by BARBULESCU and RADULESCU.

Quite different results were obtained when the Friedel-Crafts reaction was conducted in benzene solution. After pyrolysis the main products were then tetraphene, chrysene (XIV) and 1.2-3.4-dibenzopyrene (XV).



XIV

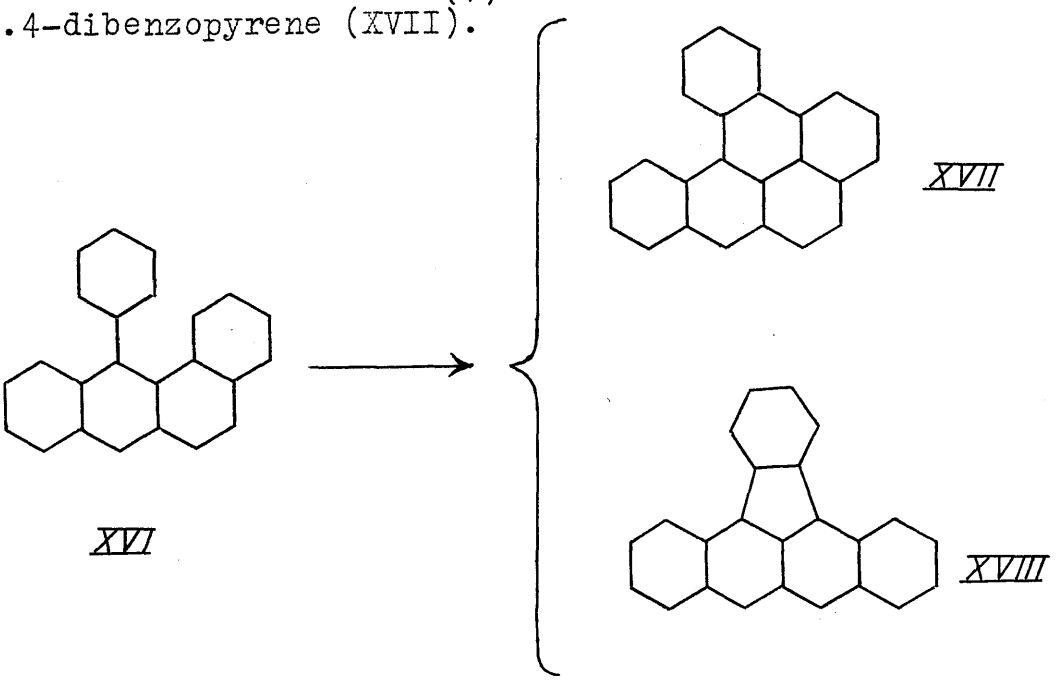


XV

The presence of the latter hydrocarbon can be explained by the preferential reaction of the solvent benzene with tetraphene. ZANDER (6) prepared this hydro-

carbon by the condensation of benzene with tetraphene in the presence of aluminium chloride. However, it is remarkable that in our case this condensation competes with the normal Friedel-Crafts reaction so successfully that no 6.7-benzopentaphene is obtained.

The presence of chrysene can be explained only by the occurrence of some type of rearrangement in the course of the reaction. Rearrangements of the tetraphene molecule are by no means uncommon. Thus, the cyclisation of 12-phenyltetraphene (XVI) gives 2.3-6.7-dibenzofluoranthene (XVIII) along with the expected 1.2-3.4-dibenzopyrene (XVII).(7)



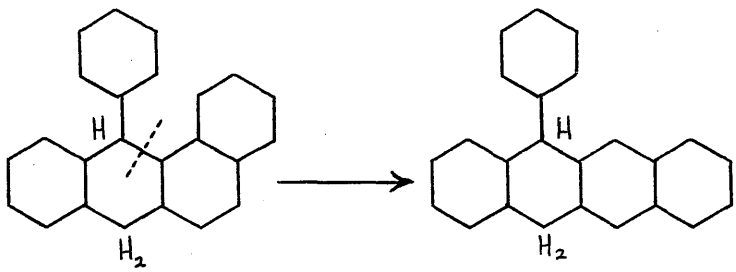
XVI

XVII

XVIII

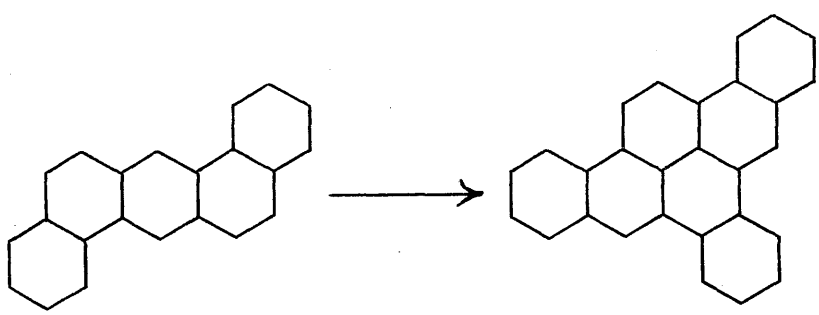
The formation of the dibenzofluoranthene may be explained by the hydrogenation of the phenyltetraphene to the compound (XIX) the hydrogen being provided by

the basic ring-closure to dibenzopyrene. Subsequent ring fission and recyclisation give the rearranged product.



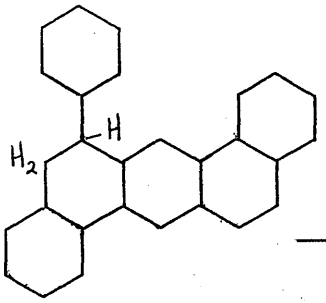
XIX

Similarly, 8.9-benzotetraphene (XX) on treatment with benzene and aluminium chloride yields 1.2-4.5-8.9-tribenzopyrene (XXI).[8]

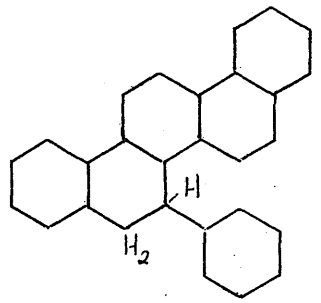


XX XXI

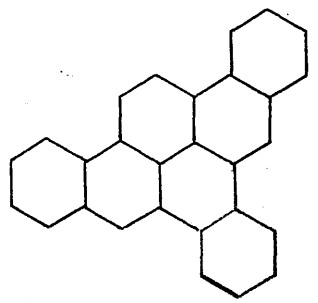
It is probable that the course of this rearrangement is similar to the above, i.e. the formation of the phenyl dihydro-compound (XXII), rearrangement to (XXIII), and ring closure followed by dehydrogenation -



XXII

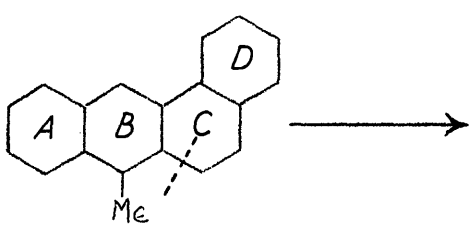


XXIII

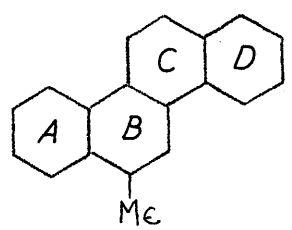


XXI

(9)
BUU-HOI and LAVIT-LAMY recently obtained 2-methyl chrysene (XXIV) by the isomerisation of 7-methyl tetraphene (XXIVa) under the catalytic influence of aluminium chloride in benzene. These authors, who consider this rearrangement to be "the first directly demonstrable example of the conversion of an anthraceno - to a phenanthreno-hydrocarbon", postulate the fission of a ring C followed by a recyclisation.



XXIVa



XXIV

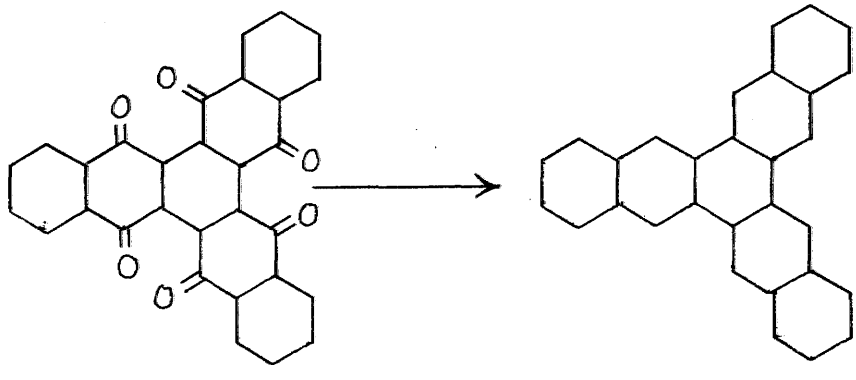
However, the fission of an aromatic C-C bond is rather unlikely and it must here again be inferred that the first step is hydrogenation followed by fission.

Another example of this type of rearrangement is the equilibrium mixture of octahydroanthracene and octahydrophenanthrene formed when octahydroanthracene is treated with aluminium chloride in benzene solution. (10)

It is of interest to note that all of these rearrangements take place in benzene solution and it may be that the benzene forms some type of intermediate adduct with the reacting hydrocarbon. The fact that no chrysene was obtained when our reaction was conducted in methylene chloride would appear to lend weight to this idea.

- - - - - - - -

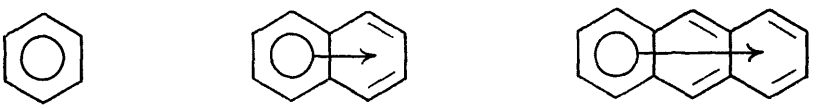
In the course of this work, an improved method of reducing the readily available triphthaloyl benzene



XXV XXVI

(XXV) to trinaphthylene (XXVI) was found.[11] This consisted of heating triphthaloyl benzene, zinc dust and a few drops of water in a sealed tube at 300° for two days. The zinc was dissolved in concentrated hydrochloric acid and the remaining black material sublimed to give colorless needles of trinaphthylene.

THEORETICAL DISCUSSION: As was stated in Chapter I (p.4), there are assumed to be two mobile and four ring-localised π-electrons in an aromatic sextet. It is the mobility of these two transferable π-electrons which explain the regular spectral shifts in the acene, phene, etc. series.[12] Thus the linear fusion of rings to benzene give the following symmetrical shifts -



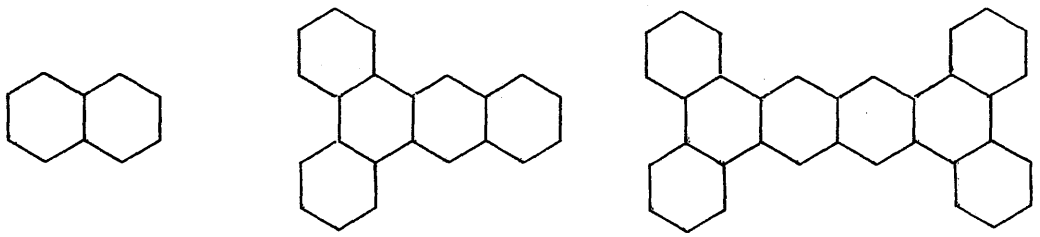
$\lambda_\beta =$ 1819 $\xrightarrow{+391}$ 2210 $\xrightarrow{+305}$ 2515 Å

$\sqrt{\lambda_\beta} =$ 42.65 $\xrightarrow{4.36}$ 47.01 $\xrightarrow{3.14}$ 50.15 $\sqrt{\text{Å}}$

That is to say, the linear annellation of butadiene units to benzene leads to a regular increment in wave-

length preferably measured in $\sqrt{}$Å, a scale for reciprocal nuclear charges.

As has already been shown in Chapter I, an asymmetric annellation effect is observed in the following type of series:



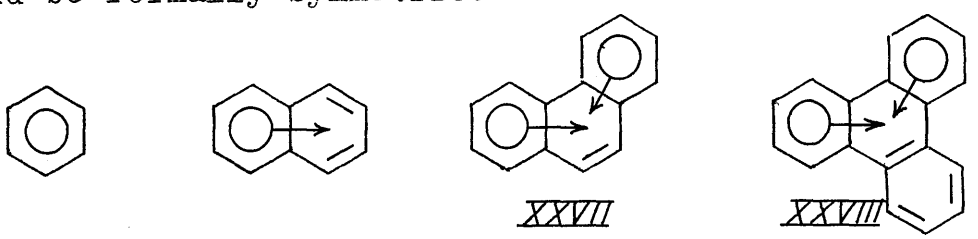
$\lambda_\beta =$ 2210 $\xrightarrow{+650}$ 2860 $\xrightarrow{+395}$ 3255 Å

$\lambda_\beta =$ 47.01 $\xrightarrow{+6.47}$ 53.48 $\xrightarrow{+3.57}$ 57.05 $\sqrt{}$Å

(13)

It is apparent that in tetrabenzotetracene, the formation of the induced π-electron sextet is preferred to a symmetric distribution of electrons as is required by resonance theory.

Another type of asymmetric annellation is observed in the following trigonal annellation which should be formally symmetric:-



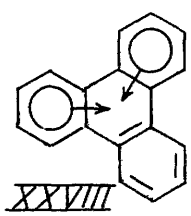
XXVII XXVIII

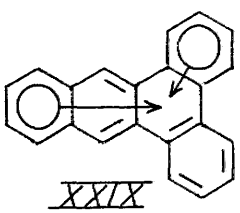
$\lambda_\beta =$ 1852 $\xrightarrow{+358}$ 2210 $\xrightarrow{+300}$ 2510 $\xrightarrow{+60}$ 2570 Å

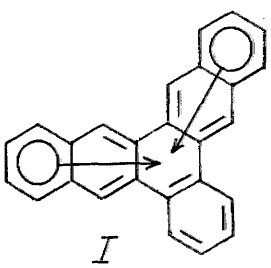
$\lambda_p =$ 2068 $\xrightarrow{+782}$ 2850 $\xrightarrow{+75}$ 2925 $\xrightarrow{-85}$ 2840 Å

In passing from benzene to naphthalene and phenanthrene the β-bands shift in much the same way as in the acene series. However, only a small shift is observed in going from phenanthrene to triphenylene.

The formulation of phenanthrene with the maximum number of aromatic sextets leads to (XXVII) in which there is a fixed double bond in the 9:10 position. The annellation of a butadiene unit to this produces a new ring with three formal double bonds and this would normally be represented by a circle for the electronic sextet. It was previously thought that the small observed shift in wavelength was caused by the formation of this new sextet. However, if this were the case there could be no other small red or violet shift on further linear annellation since no new sextet could be formed. In fact, a full linear annellation effect


XXVIII


XXIX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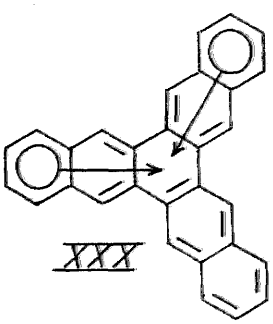
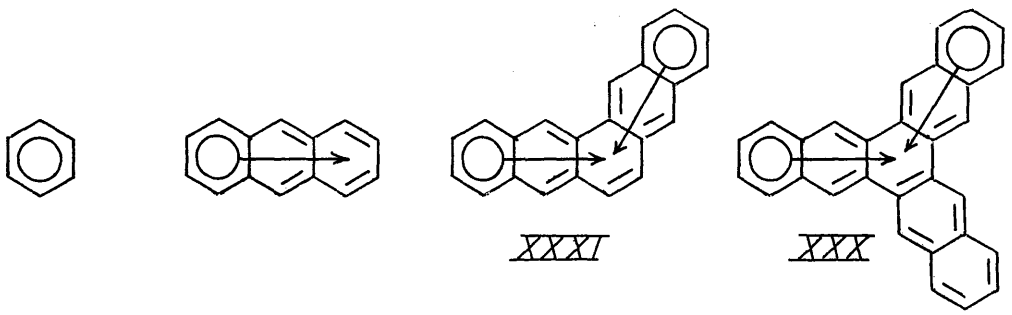

XXX

$\lambda_\beta =$ 2570 $\xrightarrow{+300}$ 2870 $\xrightarrow{+270}$ 3140 $\xrightarrow{-20}$ 3120 Å

$\lambda_p =$ 2840 $\xrightarrow{+650}$ 3490 $\xrightarrow{-100}$ 3390 $\xrightarrow{-20}$ 3370 Å

(+300 and +270Å respectively) is recorded in passing from triphenylene (XXVIII) to 1.2-3.4-dibenzanthracene (XXIX) and 6.7-benzopentaphene (I). However, further annellation to 2.3-trinaphthylene (XXX) gives a small violet shift.

This abnormal annellation effect for the third branch of the molecule is even more noticable if the following series is examined:-



XXXI XXX

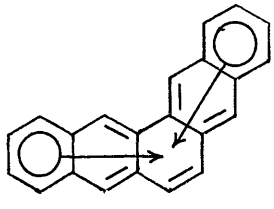
λ_β= 1852 $\xrightarrow{+663}$ 2515 $\xrightarrow{+630}$ 3145 $\xrightarrow{-25}$ 3120 Å

λ_p= 2068 $\xrightarrow{+1677}$ 3745 $\xrightarrow{-185}$ 3560 $\xrightarrow{-190}$ 3370 Å

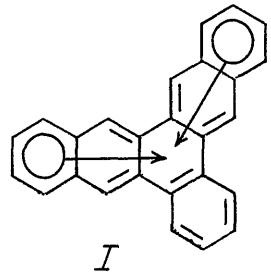
In passing from benzene to anthracene and pentaphene (XXXI) the β-bands shift by +663 and +630Å respectively, while the third annellation to trinaphthylene (XXX) gives a shift of only -25Å.

Obviously these unusually small shifts are caused, not by the formation of a new sextet, but by the fixation of the central double bonds in phenanthrene and pentaphene. If these double bonds are utilised in the

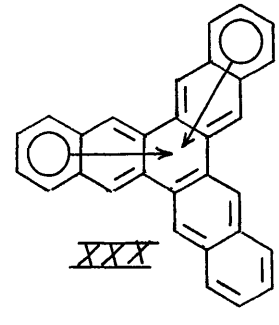
formation of an induced sextet (as marked by arrows) then they are not available for participation in a new sexter which, migrating through the third branch could produce an aromatic coupling of the whole system. It therefore appears that the double bonds in the central rings cut off the third branch of the molecules from aromatic conjugation and allow only the simultaneous coupling of two branches. Thus a formally symmetrical molecule like trinaphthalene at any instant of time must be electronically asymmetric. Accordingly, in the series pentaphene (XXXI), 6.7-benzopentaphene (I) and trinaphthylene (XXX) there should be little shift in the β-bands since the basic aromatic molecule is, in each case, pentaphene, to which has been annellated units which do not affect the β-bands.



XXXI



I



XXX

$\lambda_\beta =$ 3145 $\xrightarrow{-5}$ 3140 $\xrightarrow{-20}$ 3120 Å

$\lambda_P =$ 3560 $\xrightarrow{-170}$ 3390 $\xrightarrow{-20}$ 3370 Å

This is shown to be the case, the annellation of successive butadiene units causing, in fact, small violet shifts.

In an asymmetric hydrocarbon like 6.7-benzopentaphene it is apparent that there are two possibilities for conjugation:

(a) that the two long branches are conjugated.

or (b) that a long and a short branch are conjugated.

Thus the spectrum of the hydrocarbon should represent a super position of the spectra of pentaphene for case (a) and tetraphene for (b). As has been noted the β-band of 6.7-benzopentaphene is at 3140Å which is almost identical with that of pentaphene (3145Å). Aromatic conjugation of a long and a short branch should produce a β-band at shorter wavelength, and in accordance with this, 6.7-benzopentaphene has a β'-band at 2840Å which is much the same as the β-band of tetraphene (at 2870Å).

It may be noted that the p-bands (λ_p) show the full annellation shifts only on the elongation of the longer linear branches and exhibit small, mainly violet shifts on the extension of the shorter ones. This is believed to be due to the localisation of two π-electrons in the meso-positions of the molecules.(14)

The conclusion must be reached from the preceding argument that, of the four localised π-electrons possessed by a benzenoid ring, two must be capable of mobility within the ring while the remaining two are confined to a double bond. Thus three electronic levels are present in an acene. The highest of these is occupied by two π-electrons which can migrate through the entire system and is represented by ---

$$\frac{16R}{D^2}$$

where R is the Rydberg constant and D is the number of rings plus five.

The next lower level contains two ring-localised π-electrons and is represented by ---

$$\frac{36R}{K^2}$$

where K is half the number of rings plus seven.

The lowest level is filled with the two π-electrons confined to the double bond and is represented by ---

$$\frac{43R}{K^2}$$

Both D and K are reciprocal nuclear charges acting on these three levels and are related by the function:

$$D = 2K - 9$$

The transition of electrons from the second to the first level, $20R/K^2$ produces the α-bands while the transition from the third to the first, $27R/K^2$ produces the β-bands. The p-bands correspond to $16R/D^2$.

Thus in any benzenoid ring, there are three types of π-electrons:

(a) a completely mobile pair capable of migration out of the ring.

(b) a pair completely delocalised within the ring.

and (c) a pair confined to a double bond within the ring.

-------oOo-------

EXPERIMENTAL.

o-TOLOYL-TETRAPHENE (XIII).

Aluminium chloride (15g) was slowly added to a solution of tetraphene (20g) and o-toloyl chloride (15g) in methylene chloride (100ml), the color immediately becoming deep red with the evolution of much hydrogen chloride. The mixture was permitted to stand at room temperature for 10 minutes and then decomposed with dilute hydrochloric acid. The organic layer was thoroughly extracted with aqueous ammonia, and the methylene chloride removed by steam distillation, a red-brown resin (28g) being obtained. A sample of this was chromatographed in benzene using grade "O" alumina and the resulting pale yellow solid recrystallised from petroleum as pale yellow needles, m.p. 150-151°. These

dissolved in concentrated sulphuric acid to give a violet-red becoming orange solution.

Found: C, 89.6 ; H, 5.6

$C_{26}H_{18}O$ requires: C, 90.1 ; H, 5.2%

6.7-BENZOPENTAPHENE (I).

The crude ketone was dissolved in xylene, filtered and the xylene removed. It was then pyrolised for 20 minutes at 430-440°, the maximum temperature reached being 500°, and the dark solid obtained chromatographed in benzene/light petroleum. The major product of the eluate was a yellow solid which, after sublimation and repeated crystallisation from xylene, gave very pale yellow needles of 6.7-benzopentaphene, m.p. 250-251°, (Lit. 240°)[4]. The compound was insoluble in concentrated sulphuric acid.

Found: C, 95.2 ; H, 4.9

$C_{26}H_{16}$ requires: C, 95.1 ; H, 4.9%

6.7-BENZOPENTAPHENE-5.14-8.13-DIQUINONE (VI).

Pure benzopentaphene (0.12g) was suspended in boiling acetic acid (12ml) and a solution of chromium trioxide (0.2g) in acetic acid (8ml) slowly added. The color immediately darkened. Refluxing was continued for 12 hours and water added dropwise, the yellow solid obtained crystallising from xylene as bright yellow needles of the diquinone, m.p. 285-286°. (Lit. 286-287°)[4]. The compound gave a yellow-red solution with concentrated sulphuric acid and an orange-red vat with alkaline dithionate.

Found: C, 80.7 ; H, 3.5

$C_{26}H_{12}O_4$ requires: C, 80.4 ; H, 3.1%

AZINE FROM ABOVE (XII).

A boiling solution of the diquinone (32mg) in pyridine (2ml) was treated with hydrazine hydrate (6 drops) and the violet solution refluxed for 1 hour. It was then acidified with dilute hydrochloric acid and the bluish solid purified by vat-formation. The red flakes of azine were recrystallised from xylene as deep red needles, m.p. 307-308° (Lit. 310°)[4] with decomposition which gave a violet coloration with con-

centrated sulphuric acid.

Found: N, 7.4

$C_{26}H_{12}O_2N_2$ requires: N, 7.3%

REACTION IN BENZENE.

Tetraphene (34g) and o-toloyl chloride (25g) were dissolved in benzene (150ml) at 0° and aluminium chloride (25g) added. The color of the mixture immediately became claret, but after about 10 minutes was orange-red. It was decomposed in dilute hydrochloric acid and the benzene removed by steam distillation. The beige solid (55g) obtained was thoroughly washed with water and aqueous ammonia, dissolved in xylene and filtered. The solution was concentrated and the solid obtained was pyrolised for 55 minutes.

After sublimation and chromatography, only chrysene, m.p. 254-255° (Lit. 255-256°) and 1.2-3.4-dibenzopyrene, m.p. 225° (Lit. 224-226°)[4] could be isolated. These were identified by their UV absorption spectra.

2.3-TRINAPHTHYLENE (XXVI).

Triphthaloyl benzene (2g) was ground with zinc dust (15g) and placed in a Carius tube with 3 drops of water. The tube was evacuated and sealed and then heated at 300° for 48 hours. The mixture was treated with concentrated hydrochloric acid and the resulting dark powder (1.85g) filtered off and washed with ammonia and water. This was then sublimed at 300° and 10^{-2} mm when cream needles were obtained. These crystallised from xylene as long colorless needles (0.8g), m.p. 390-391° (Lit. 392° [11]).

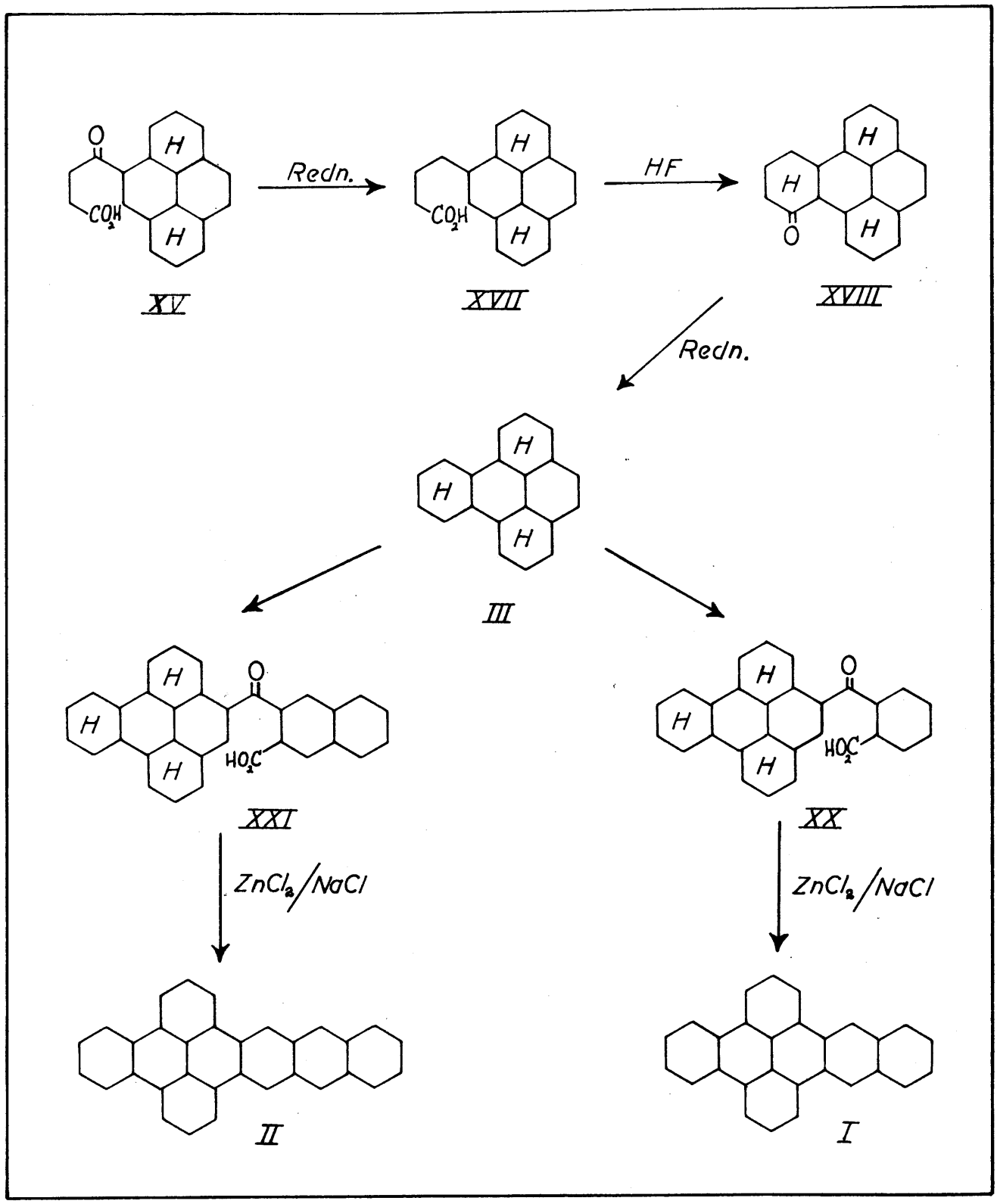
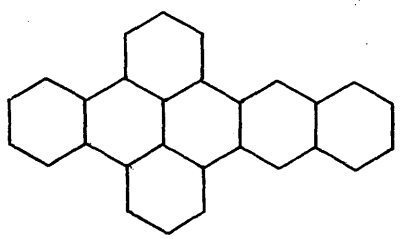


FIGURE V.

Flow-sheet for Chapter III.

C H A P T E R III.

1.2-BENZO-NAPHTHO-[2".3"-7.8]-PYRENE and 1.2-BENZO-ANTHRACENO-[2".3"-7.8]-PYRENE.



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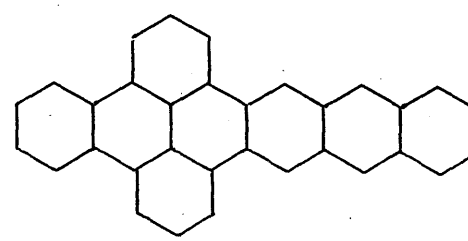
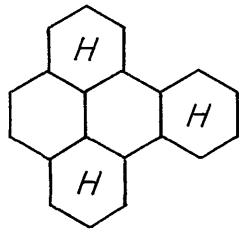


II

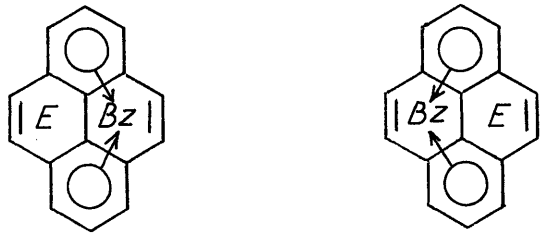
INTRODUCTION: While many benzologues of pyrene are known, few of these are annellated in the 1.2 and 7.8 positions.[1][2][3] Accordingly the systematic synthesis of these linear pyrenes has now been initiated, and the preparation of benzo-naphthopyrene (I) and benzo-anthracenopyrene (II) is part of this work. Both of these hydrocarbons are

readily available from the hitherto unknown 3,4,5,8,9, 10,1',2',3',4'-decahydro-1,2-benzopyrene (III).



III

THEORETICAL DISCUSSION: The ideas outlined in Chapters I and II may be applied to the linear pyrene series. Considering pyrene (IV) itself, it is obvious that in the central naphthalene unit there can be only one induced benzenoid ring formed

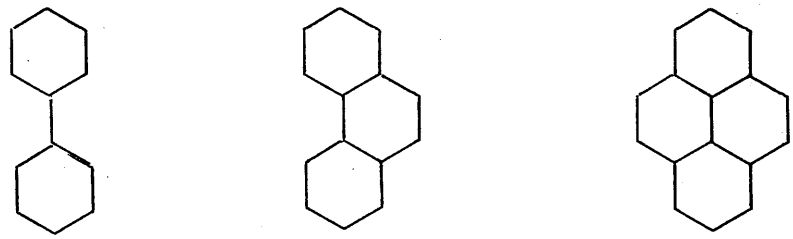


a b

IV

at any one moment by the donation of π-electrons from the adjacent rings. Thus the situations in IVa and IVb are possible. That this distribution of π-elec-

trons is actually present in pyrene may be shown by consideration of the annellation of ethylene units to diphenyl:

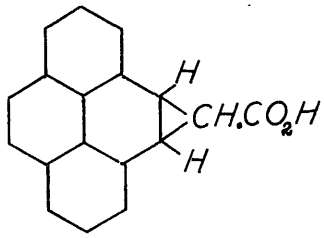


λ_β = 2100 $\xrightarrow{+430}$ 2530 $\xrightarrow{+210}$ 2740 Å

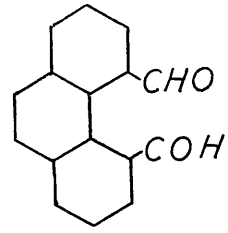
$\sqrt{\lambda_\beta}$ = 45.83 $\xrightarrow{4.47}$ 50.30 $\xrightarrow{2.05}$ 52.35 $\sqrt{\text{Å}}$

The second shift is asymmetric and hence one of the central rings must be empty while the other has induced benzenoid character.(4)

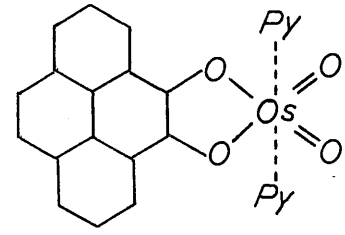
The bonds in the 1.2 and 6.7 positions may be shown to possess much double bond character since pyrene reacts with ethylenic reagents in these positions. Thus with diazoacetic ester the compound (V) is formed;(5) with ozone(6), the compound (VI) and with osmium tetroxide(7), the compound (VII).



V



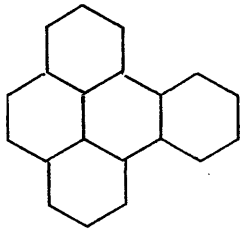
VI



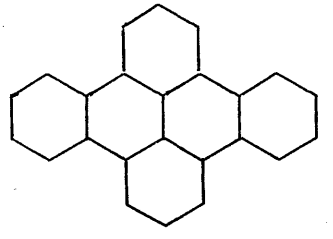
VII

In contrast to this, in the Friedel-Crafts reaction and with ionic reagents such as Br^+ and NO_2^+, pyrene reacts at the 3, 5 and 10 positions.[8] However, this reactivity originates from the localisation of π-electrons at these points - a fact which is also responsible for the p-band absorption.[9]

The electronic structure assigned to pyrene may be extended to the other members of the series. Thus 1.2-benzopyrene (VIII) and 1.2-6.7-dibenzopyrene (IX) would be represented by -

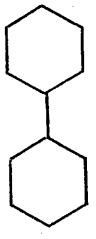


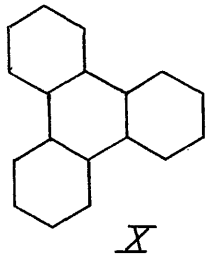
VIII



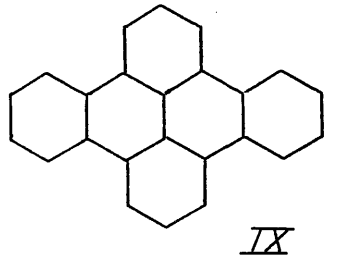
IX

That these structures are correct may be seen by consideration of the series, diphenyl, triphenylene (X) and dibenzopyrene (IX):[10]





X



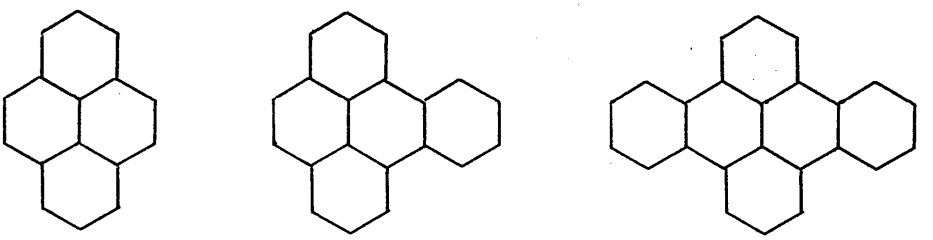
IX

λ_β = 2100 $\xrightarrow{+490}$ 2590 $\xrightarrow{+300}$ 2890 Å

$\sqrt{\lambda_\beta}$ = 45.83 $\xrightarrow{5.06}$ 50.89 $\xrightarrow{2.87}$ 53.76 $\sqrt{\text{Å}}$

(11)

and also of the series:



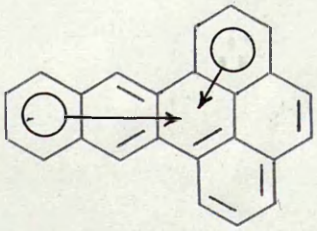
VIII IX

$$\lambda_\beta = \quad 2740 \xrightarrow{+170} 2910 \xrightarrow{-20} 2890 \ \text{Å}$$

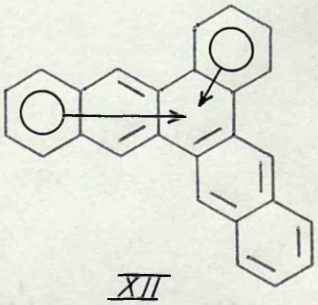
$$\sqrt{\lambda_\beta} = \quad 52.35 \xrightarrow{+1.59} 53.94 \xrightarrow{-0.18} 53.76 \ \sqrt{\text{Å}}$$

Both of these second shifts are small and obviously they constitute asymmetric annellations. Hence the structures of benzopyrene and dibenzopyrene would appear to be as stated.

By the simple treatment described in Chapter I, the small shift in the β-band on going from (VIII) to (IX) would be ascribed to the usual minor effect obtained on annellation of a butadiene unit to the formally fixed double bond in benzopyrene (VIII). However, the more refined theory of Chapter II provides more information on the underlying electronic movements. The situation in 1.2-naphthopyrene (XI) is in fact very similar to that in 6.7-benzopentaphene (XII).

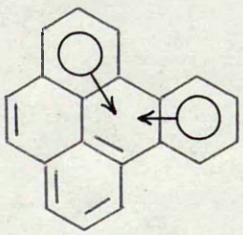


XI

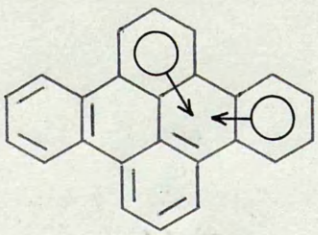


XII

Hence it is obvious that here again only two-branch conjugation can occur at any moment. Thus dibenzopyrene and benzopyrene would be written:



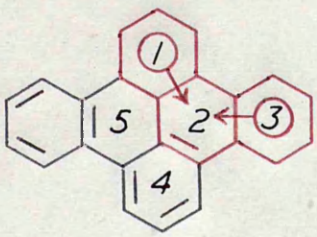
VIII



IX

It may be seen that the maximum possible conjugation in each of these is equivalent to that of phenanthrene and hence the close agreement of the β-bands.

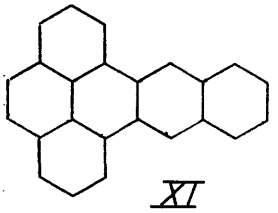
Considering dibenzopyrene (IX) in more detail:



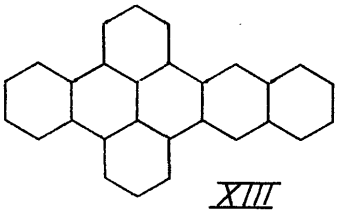
IX

Two π-electrons are donated by each of the benzenoid rings 1 and 3 to the ring 2. These, together with the two lowest level π-electrons provided by ring 2, confer induced benzenoid character upon ring 2. Hence, since ring 4 has lost these "base" electrons, it is cut off from conjugation with the rest of the unit. Ring 5, since it is empty, cuts off the remaining part of the molecule. Hence the molecule should have the approximate conjugation of phenanthrene connected with single bonds.

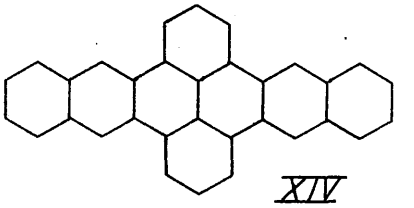
That this is the case may be further shown by the comparison of naphthopyrene (XI), benzonaphthopyrene (XIII) and dinaphthopyrene (XIV):



XI



XIII

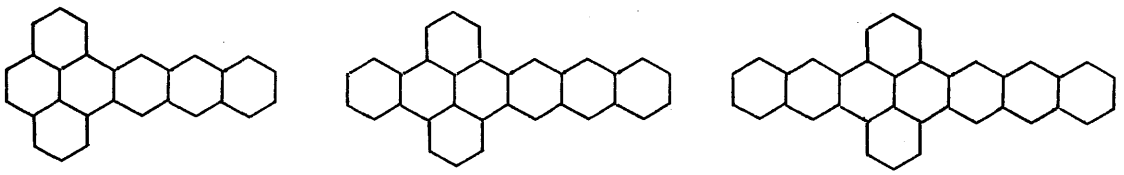


XIV

$$\lambda_\beta = 3180 \xrightarrow{-20} 3160 \xrightarrow{-20} 3140\ \text{Å}$$

Here again the basic conjugative unit is the same, and the β-bands are correspondingly similar.

Another series of the same type shows the same striking correspondence of the β-bands:

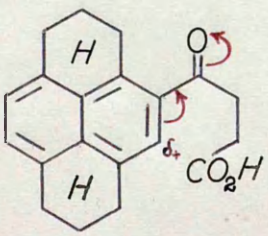


λ_β = 3555 $\xrightarrow{-75}$ 3480 $\xrightarrow{-40}$ 3440 Å

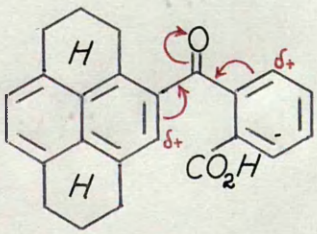
Hence, this Chapter confirms the conclusions reached in Chapter II that the six π-electrons in a benzene ring are indeed distributed in pairs in the discrete energy levels.

-------oOo-------

EXPERIMENTAL DISCUSSION: Under the conditions of the Friedel-Crafts reaction, 3,4,5,8,9,10-hexahydropyrene reacts as an alkylated naphthalene. Hence, with succinic anhydride, the keto-acid (XV) was obtained in good yield. This cannot be directly ring-closed to the quinone, in contrast to the facile cyclisation of the phthalic derivative (XVI), (vide Chapter V p. 86) The explanation of this failure is presumably that in (XVI), the benzene ring of the carboxybenzoyl group acts as an electron sink and hence the deactivating effect of the carbonyl group is minimised. Thus:



XV



XVI

The keto-acid (XV) was accordingly reduced before cyclisation. Two methods of reduction were used - Clemmensen reduction and Huang-Minlon reduction, but the former was found to provide slightly better yields of the γ-pyrenyl butyric acid (XVII).

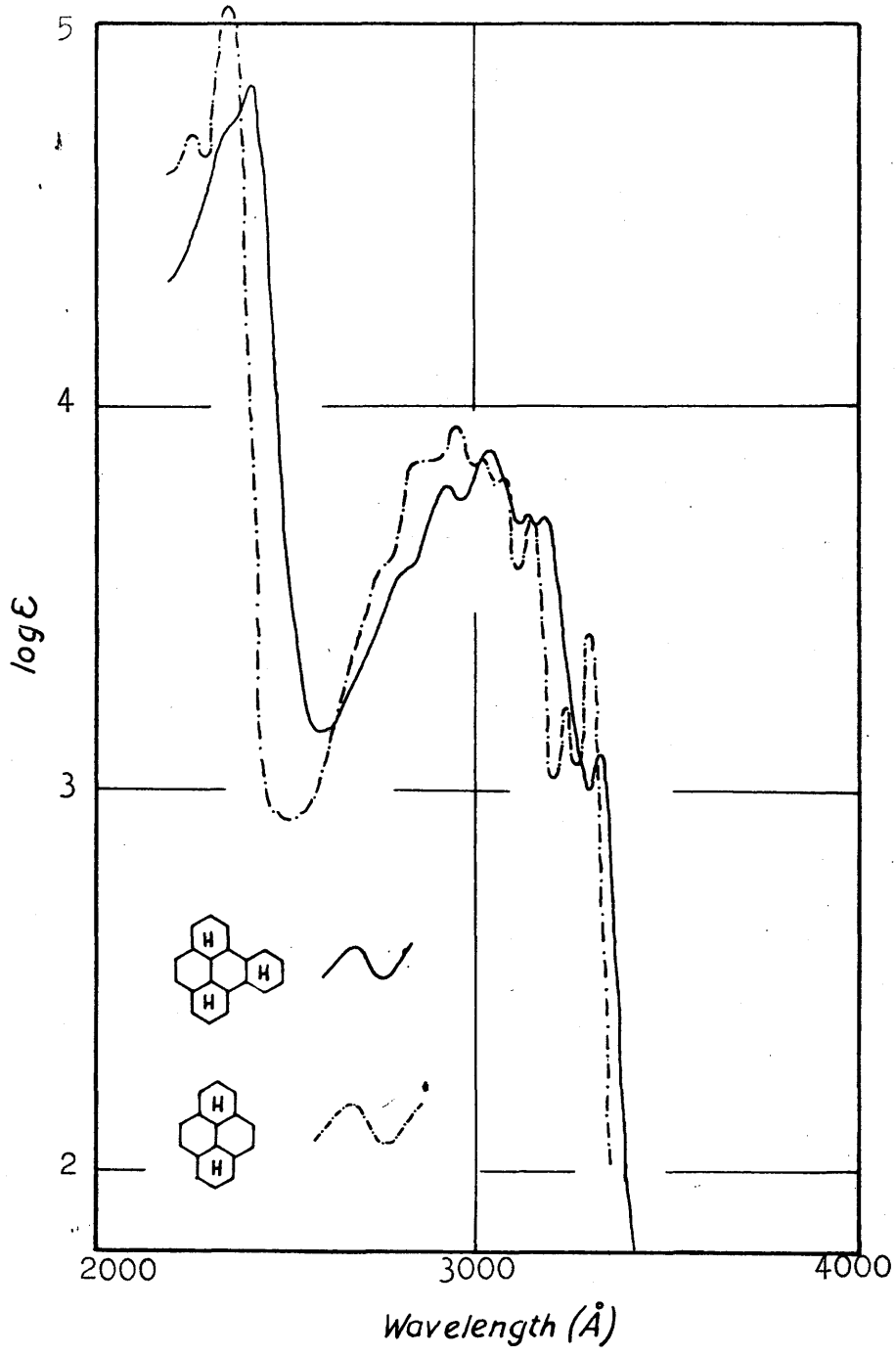


FIGURE VI. Absorption max. (Å) and logε (in parentheses). 3,4,5,8,9,10,1,2,3,4-Decahydro-1.2-benzopyrene (III) in cyclohexane, β:2400(4.85); p:2920(3.80), 3040(3.89), 3140(3.72); α 3330(3.09).
3,4,5,8,9,10-Hexahydropyrene in heptane, β:2250(4.71), 2350(5.05); p:2875(3.85),2975(3.95), 3025(3.86), 3100(3.80), 3150(3.71); α :3240(3.21), 3300(3.40).

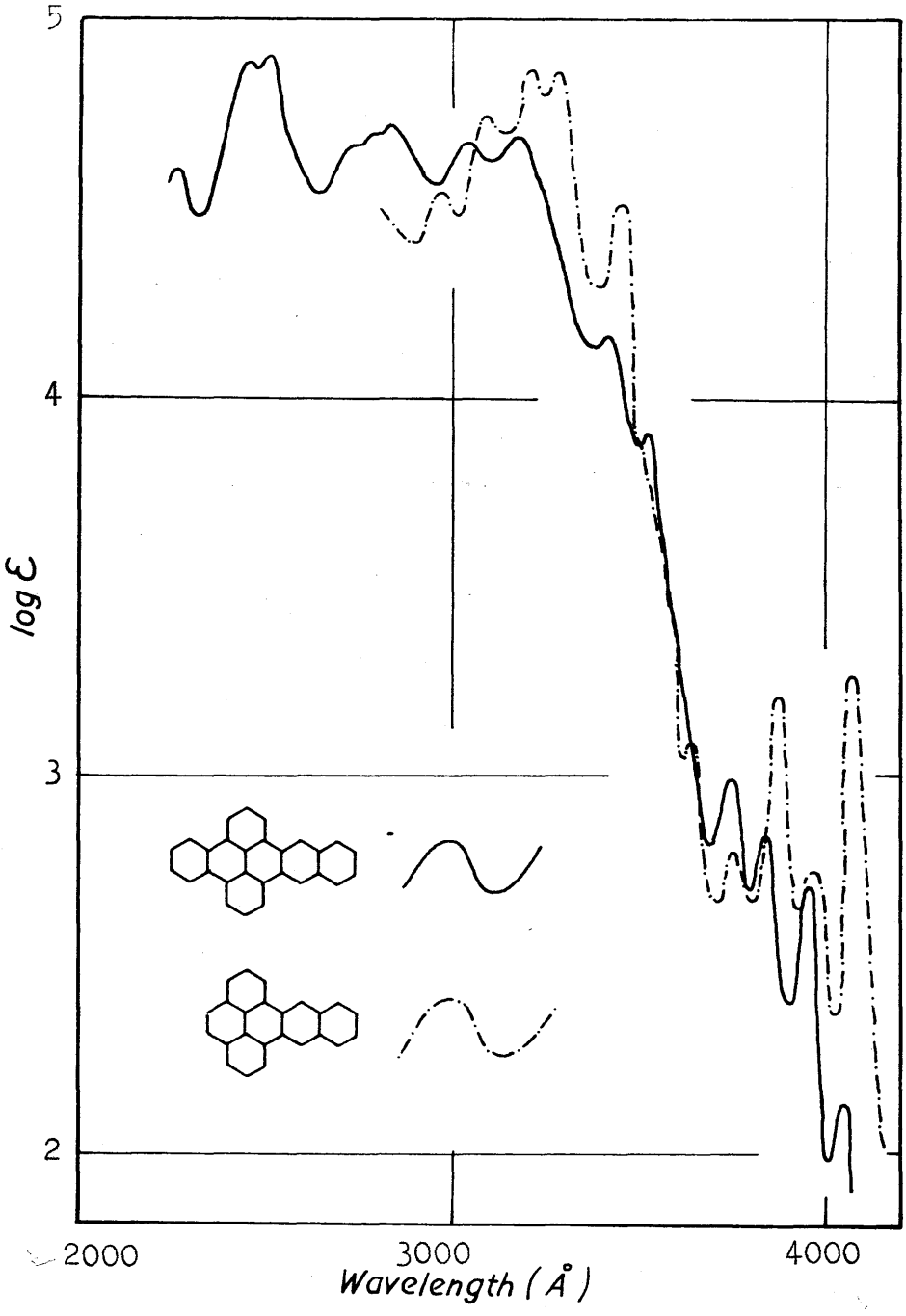


FIGURE VII. Absorption max. (A) and log (in parentheses). 1.2-Benzo-naphtho-[2".3"-7.8]-pyrene (I) in benzene, α : 4050 (2.13), 3955 (2.70), 2840 (2.84), 2750 (2.90); p : 3520 (3.90), 3420 (4.18); β :3170 (4.70), 3040 (4.68); β': 2840 (4.73), 2730 (4.67); β": 2520 (4.91), 2450 (4.90).
Naphtho-[2'.3'-1.2]-pyrene in benzene, α :4075 (3.26), 3960 (2.74), 3860 (3.20), 3750 (2.80), 3670 (3.08); p : 3450 (4.52); β: 3280 (4.85), 3210 (4.85),3090 (4.74), 2970 (4.53).

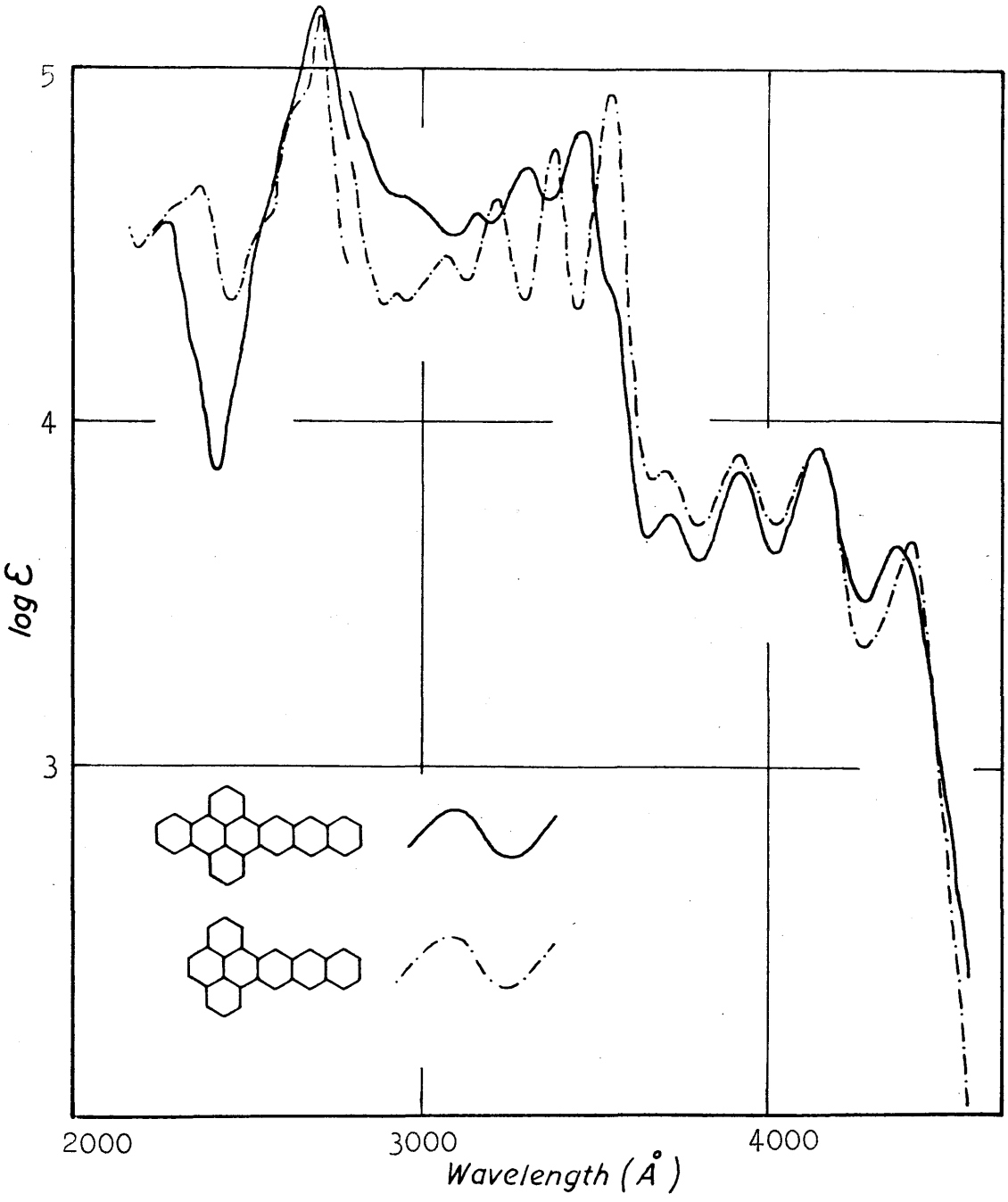
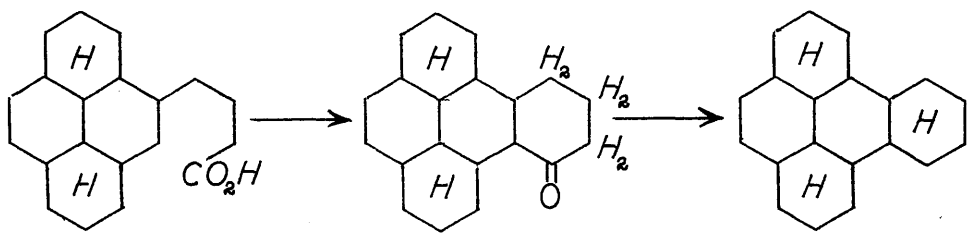


FIGURE VIII. Absorption max. (Å) and logε (in parentheses). 1.2-Benzo-anthraceno-[2".3"-7.8]-pyrene (II) in benzene, p : 4370 (3.63), 4150 (3.91), 3920 (3.84), 3720 (3.72); β : 3480 (4.82), 3310 (4.72), 3160 (4.59); β': 2700 (5.18). From 2800Å in cyclohexane. Anthraceno-[2'.3'-1.2]-pyrene in benzene, p : 4410 (3.65), 4150 (3.92), 3920 (3.90), 3700 (3.85); β : 3555 ((4.93), 3380 (4.77), 3210 (4.63), 3070 (4.47), 2930 (4.36); β': 2700 (5.15). From 2800Å in cyclohexane.

Ring closure of this γ-pyrenyl butyric acid with anhydrous hydrogen fluoride led to the dodecahydrotriphenylene ketone (XVIII), and Clemmensen reduction of this to the previously unknown hydrocarbon decahydro-1.2-benzopyrene (XIX), the absorption spectrum of which is shown in Figure VI.



XVII XVIII XIX

The first three steps of this synthesis have already been described by COOK and HEWETT (12) but the modifications introduced here have led to a general improvement in yields.

The two keto-acids (XX) and (XXI) were obtained by Friedel-Crafts reaction of decahydrobenzopyrene with phthalic anhydride and naphthalene dicarboxylic acid anhydride respectively. A zinc chloride/sodium chloride melt on each of these gave readily the colorless benzonaphthopyrene (I) and the orange-yellow benzo-anthracenopyrene (II), the absorption spectra of which are given in Figures VII and VIII.

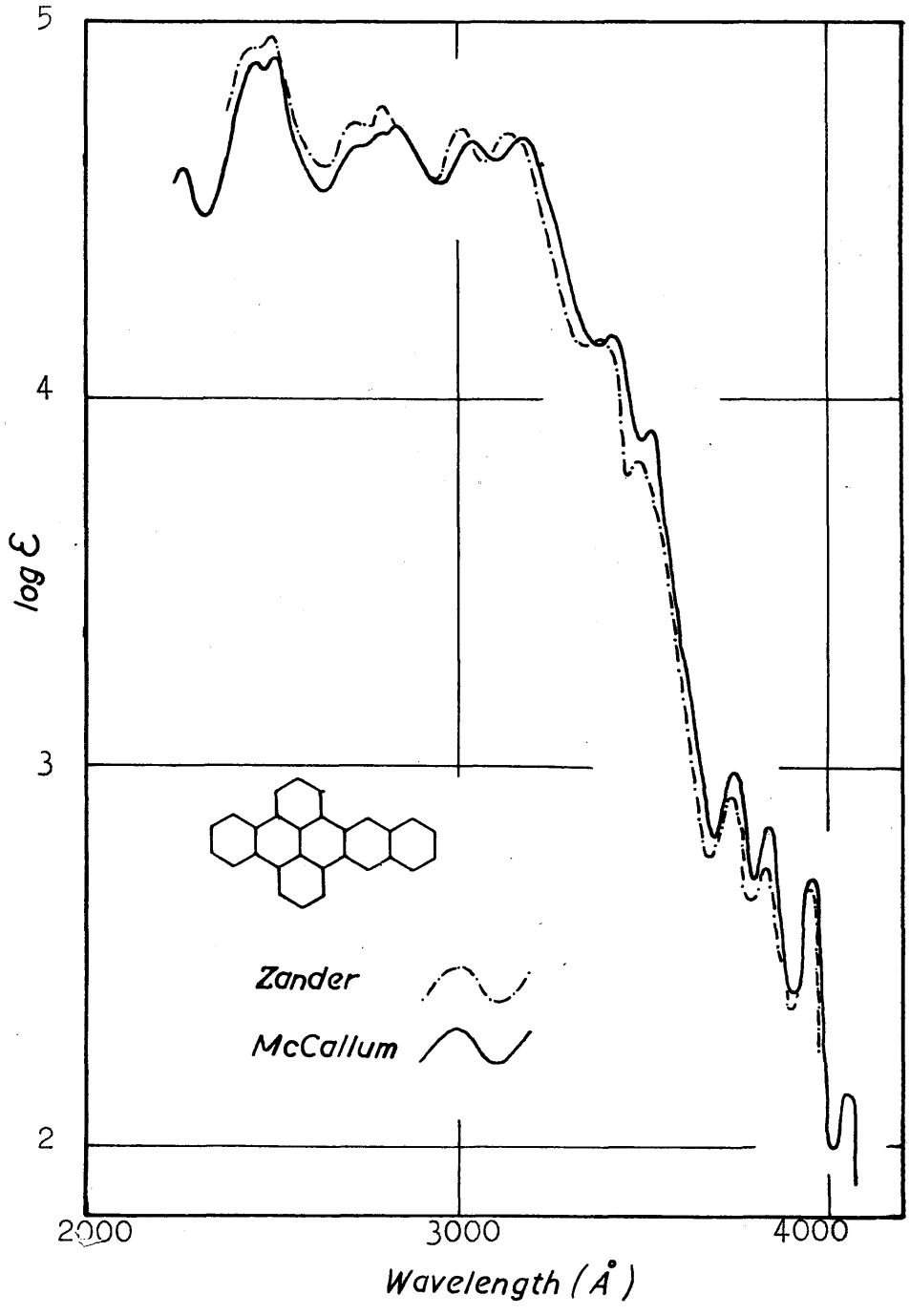
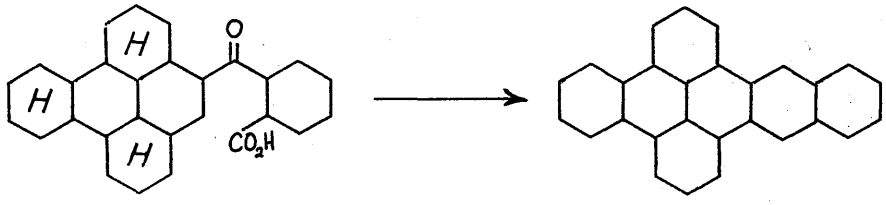
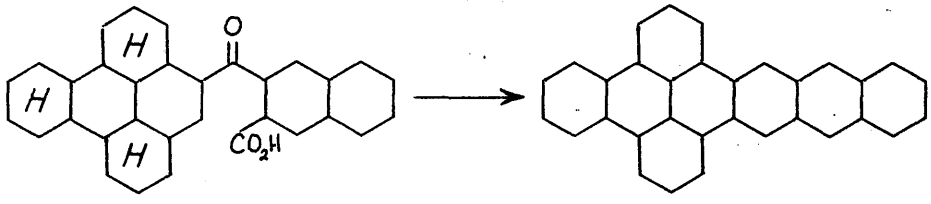


FIGURE IX.

Comparison between the 1.2-benzo-naphtho-[2".3"-7.8]-pyrene obtained in the present synthesis and that obtained by CLAR and ZANDER (13).

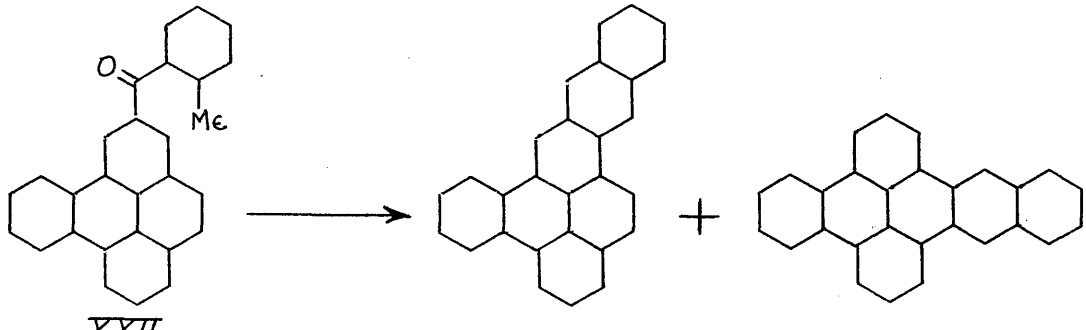


XX I



XXI II

1.2-benzo-[2".3"-7.8]-naphthopyrene (I) has recently been obtained by CLAR and ZANDER[13] as a by-product in the pyrolysis of the ketone (XXII) which was obtained by the treatment of 1.2-benzopyrene with o-toloyl chloride in the presence of aluminium chloride. A comparison of the spectra of this compound with the material obtained in the present synthesis is shown in Figure IX. It is obvious that they are practically identical.



XXII

EXPERIMENTAL.

/3-3.4,5.8,9.10-HEXAHYDRO-PYRENOYL PROPIONIC ACID (XV).

Hexahydropyrene (41.6g) and succinic anhydride (20g) were dissolved in benzene (100ml) and aluminium chloride (50g) added. The carmine mixture was agitated for 2 hours at room temperature and decomposed with dilute hydrochloric acid and ice. The pale brown solid obtained was dissolved in dilute potassium hydroxide and the hot, filtered solution on acidification yielded a brown material (52g) which crystallised from xylene as colorless needles, m.p. 178-179.5°
(Lit. 173.5° [12]). These dissolved in concentrated sulphuric acid to give violet becoming blue solution which went red on standing.

γ-3.4,5.8,9.10-HEXAHYDRO-PYRENYL BUTYRIC ACID (XVII).

Clemmensen Reduction.[14]

Amalgamated zinc wool (50g) was covered with concentrated hydrochloric acid (30ml), acetic acid (30ml) and xylene (25ml). The pure keto-acid (5g) was added to the xylene layer and the mixture refluxed for 6 hours, two 10ml. aliquots of concentrated hydrochloric acid being added at intervals. The xylene layer was removed and distilled to dryness, the white material (4.6g) obtained crystallising from benzene as colorless needles, m.p. 131-132°
(Lit. 133-134°)[12]. These dissolved in concentrated sulphuric acid to give a violet-red becoming red-brown solution.

Huang-Minlon Reduction.

A solution of the keto-acid (6g) and 100% hydrazine hydrate (3.5g) in diethylene glycol (100ml) was refluxed at 190° for 6 hours with potassium hydroxide (4g). After dilution and acidification, a white precipitate (5.1g) of the acid was obtained.

After crystallisation from benzene, this proved identical with the product obtained in the previous reaction.

1'-KETO-3,4,5,8,9,10,1',2',3',4'-DECAHYDRO-1.2-BENZOPYRENE (XVIII).

The above butyric acid (5g) was added to anhydrous hydrogen fluoride (200ml). After 3 hours, the red-violet solution was decomposed with ice-water and the resulting yellow material was crystallised from methanol to give long colorless needles (3.9g), m.p. 145-145.5° (Lit. 147-148°[12]). The compound with concentrated sulphuric acid gave a violet-red solution.

1',2',3',4',3,4,5,8,9,10-DECAHYDRO-1,2-BENZOPYRENE (XIX).

Concentrated hydrochloric acid (30ml), acetic acid (30ml), and xylene (25ml) were added to amalgamated zinc wool (50g). The above ketone (5g) was added to the xylene layer and the mixture refluxed for 6 hours, two 10ml. portions of concentrated hydrochloric acid being added during this period. The xylene was removed and concentrated. The re-

sulting white material (4.6g) crystallised from cyclohexane as very large, colorless rods, m.p. 196-197°. These were insoluble in concentrated sulphuric acid and gave no coloration on prolonged standing, the crystal surface becoming brown.

Found: C, 91.35 ; H, 8.82

$C_{20}H_{22}$ requires: C, 91.55 ; H, 8.45%

6-o-CARBOXYBENZOYL-DECAHYDRO-1.2-BENZOPYRENE (XX).

3,4,5,8,9,10,1',2',3',4'-Decahydro-1.2-benzopyrene (4.4g) and phthalic anhydride (2.2g) were dissolved in benzene (60ml) with slight warming. The addition of aluminium chloride (16g) caused the color to become deep claret and hydrogen chloride was evolved. After agitation for 1 hour at 40°, the mixture was decomposed with dilute hydrochloric acid and a beige solid obtained. This was dissolved in dilute ammonium hydroxide and the hot, filtered solution treated with hydrochloric acid. The resulting dark yellow material crystallised from benzene as small yellow blades, m.p. 237-238° and dissolved in

concentrated sulphuric acid to give a red-violet going to red-brown coloration.

Found: C, 82.13 ; H, 6.47

$C_{28}H_{26}O_3$ requires: C, 81.92 ; H, 6.39%

1.2-BENZO-NAPHTHO-[2".3"-7.8]-PYRENE (I).

The above keto-acid (1g) was ground with sodium chloride (1g) and zinc chloride (5g) and heated at 310° for 2 minutes, the color becoming dark red. The mixture was decomposed with water and the resulting black solid ground with copper powder and sublimed at 350° and 10^{-2} mm. The dark yellow oil obtained was dissolved in benzene and the solution was repeatedly extracted with concentrated sulphuric acid. The solution was then thoroughly washed with water, with ammonia and again with water, and the benzene solution was concentrated to give long colorless needles of benzo-naphtho-pyrene, m.p. 316-317° (Lit. 300-301°)[13]. These were insoluble in concentrated sulphuric acid.

Found: C, 95.1 ; H, 4.5

$C_{28}H_{16}$ requires: C, 95.4 ; H, 4.6%

6-CARBOXYNAPHTHOYL-DECAHYDRO-1.2-BENZOPYRENE (XXI).

3,4,5,8,9,10,1',2',3',4'-Decahydro-1.2-benzopyrene (3.9g) and naphthalene dicarboxylic acid anhydride (3g) were suspended in benzene and aluminium chloride (12g) added. The color became violet-red and hydrogen chloride was evolved. After agitation at 70° for 1½ hours the mixture was decomposed with dilute hydrochloric acid. The yellow resin obtained was dissolved in dilute sodium hydroxide and the hot filtered solution acidified with hydrochloric acid. The resulting beige solid (4.5g) crystallised from acetic acid as small yellow blades, m.p. 240-242° and dissolved in concentrated sulphuric acid to give a violet-red solution.

Found: C, 84.20 ; H, 6.21

$C_{32}H_{28}O_3$ requires: C, 83.45 ; H, 6.13%

1.2-BENZO-ANTHRACENO-[2".3"-7.8]-PYRENE (II).

The above keto-acid (1g) was ground with sodium chloride (1g) and zinc chloride (5g) and heated at 320° for 3 minutes the color becoming yellow-brown. The mixture was decomposed with dilute acetic acid and the resulting dark brown solid ground with copper

powder and sublimed at 350° and 10^{-2} mm. The yellow material obtained crystallised from trichlorobenzene as orange yellow needles, m.p. 372-373°, and slowly dissolved in concentrated sulphuric acid to give a brown solution which overnight became green.

Found: C, 95.59 ; H, 4.38

$C_{32}H_{16}$ requires: C, 95.49 ; H, 4.51%

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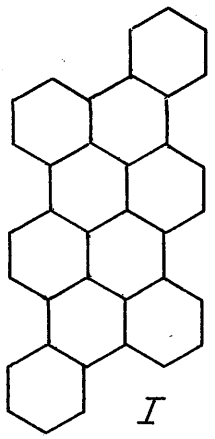
C H A P T E R IV.

1.12-2.3-6.7-8.9-TETRABENZANTHANTHRENE.[1]



I

INTRODUCTION: As was mentioned in Chapter I, hydrocarbons which can be written as containing exclusively aromatic sextets are known as fully benzenoid hydrocarbons or alternatively as condensed polyphenyls. Tetrabenzanthanthrene (I) belongs to this important class of compounds, and consequently exhibits all their expected properties.[2]

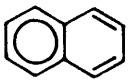
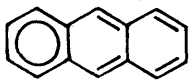
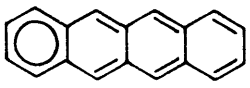
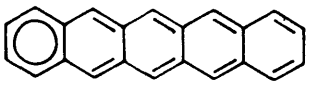
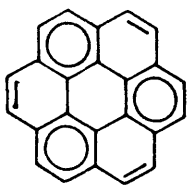
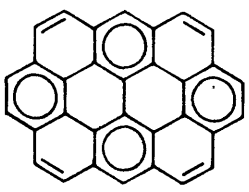
THEORETICAL DISCUSSION: The condensed polyphenyls show great similarities in their chemical and physical properties and are readily distinguishable from isomeric hydrocarbons not having their construction principle. They therefore represent a characteristic series of hydrocarbons just as do the acenes, phenes, rylenes, etc.

All of these hydrocarbons are marked by very low reactivity and high stability, and they do not dissolve in concentrated sulphuric acid to form solutions of the protonated molecules. They show very strong phosphorescence of long life in solid solution at low temperature, and their absorption spectra are the most strongly shifted to the violet of all their isomers, except for the corresponding polyphenyls.

The preceding facts indicate that a particularly stable electronic system must be present in these fully benzenoid hydrocarbons and the hypothesis that all the π-electrons can be considered as mainly confined to certain rings in inherent sextets accounts well for their observed properties.

This localisation of the π-electrons is at variance with the quantum mechanical concept of com-

TABLE 1.

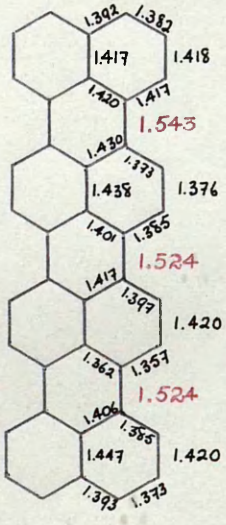
Hydrocarbon	Average π-orbital radius Å	Length Å
	1.44	2.43
	1.57	4.85
	1.65	7.27
	1.69	9.71
	1.71	12.14
	1.94	7.27
	2.12	9.71

plete delocalisation of the π-electrons in molecular orbitals. However, magnetic anisotropy measurements indicate that there is, in fact, considerable localisation of the π-electrons in polycyclic systems. Thus in the acene series, AKAMATU and MATSUNAGA[3] have shown that localisation increases with the number of linearly condensed rings, and that pentacene which is 12.14Å long has an average π-orbital radius of only 1.71Å. Table 1 shows the comparison of π-orbital radii with molecular length for a few hydrocarbons. Significantly higher values are obtained for the radii of coronene and ovalene, as in these, the presence of several sextets facilitates the migration of π-electrons.

PAUNCZ and COHEN[4] have recently examined several of these fully benzenoid compounds from the molecular orbital stand-point and their findings appear to confirm the existence of inherent sextets linked by quasi-single bonds.

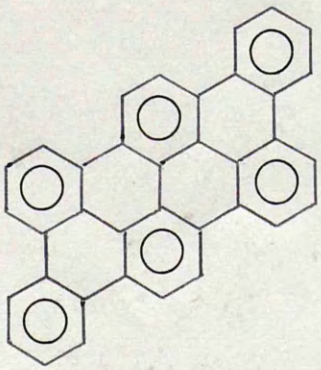
Studies of the bond-lengths of polycyclic hydrocarbons lend weight to this picture of incomplete delocalisation. Thus the X-ray analysis of quaterry-

lene (5) provided the values shown below:-



The bonds between the naphthalene units have an average length of 1.527Å and it is obvious that these are almost pure single bonds. Thus there can be little delocalisation in this molecule except between the individual rings of the naphthalene units.

These facts tend to confirm that the condensed polyphenyls consist of benzenoid rings linked by quasi-single bonds. Thus tetrabenzanthanthrene may be written -



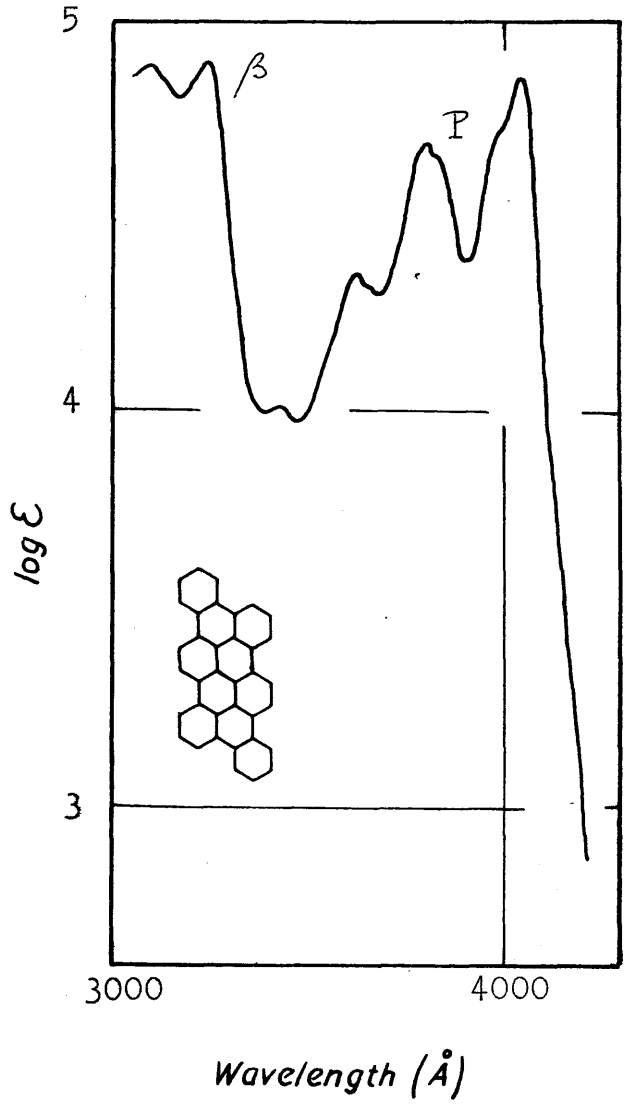
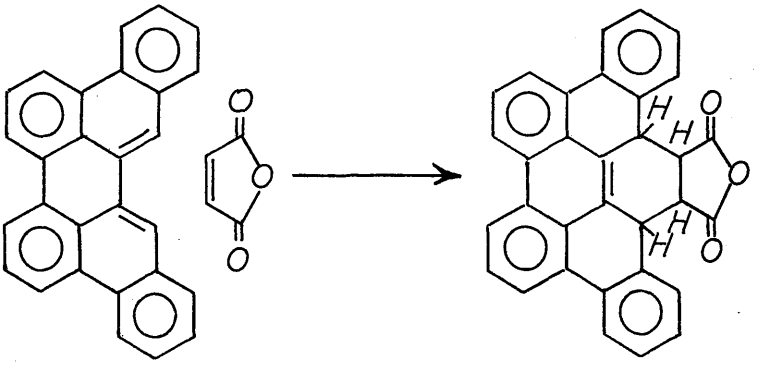


FIGURE X. Absorption max. (Å) and log (in parentheses). 1.12-2.3-6.7-8.9-Tetrabenzanthanthrene (I) in trichlorobenzene, β: 3090 (4.88), 3240 (4.89); p: 3620 (4.35), 3800 (4.69), 4040 (4.86).

Tetrabenzanthanthrene (I) may be taken as representative of the condensed polyphenyls. It is a pale yellow hydrocarbon which does not dissolve in concentrated sulphuric acid and which shows an orange phosphorescence of very long life in solid solution at low temperature. It may be sublimed repeatedly at 450° without decomposition, and its absorption spectrum as shown in Figure X is seen to be strongly shifted to the violet.

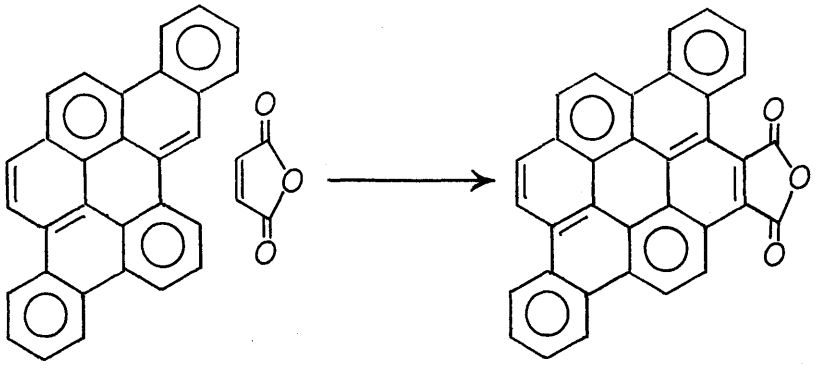
The principle of formulating condensed polyphenyls with the maximum number of sextets may be extended to polycyclic systems in general. An aromatic hydrocarbon will, of course, tend to exist in the state of lowest energy and this is the state which contains the maximum number of benzenoid rings. It may be shown that while this mode of formulation does not represent all possible arrangements of the constituent double bonds of a molecule, it certainly embraced the majority of the Kekule structures. Thus, formulating the dibenzoperylene (II)[6] with the maximum number of benzenoid rings, it is apparent that there is a butadiene unit in the molecule. Hence the reaction of (II) with dienophiles would be expected. In fact, dibenzoperylene (II) reacts with

maleic anhydride to give the adduct (III) quantitatively.



II III

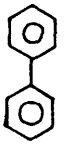
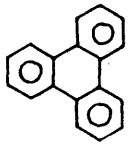
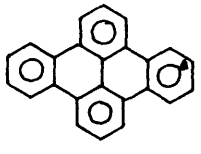
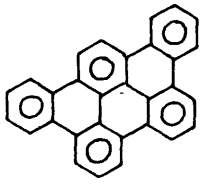
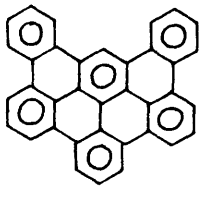
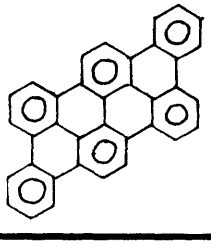
The principle may also be employed to predict the reactive positions in molecules and their stability. Thus, if the two isomeric tribenzoperylenes (IV)[7] and (V)[6] are considered, it is obvious that (IV) contains a styrene unit and hence would be expected to react with dienophiles while (V) is seen to be fully benzenoid and consequently chemically inert. These predictions are borne out experimentally, (IV)

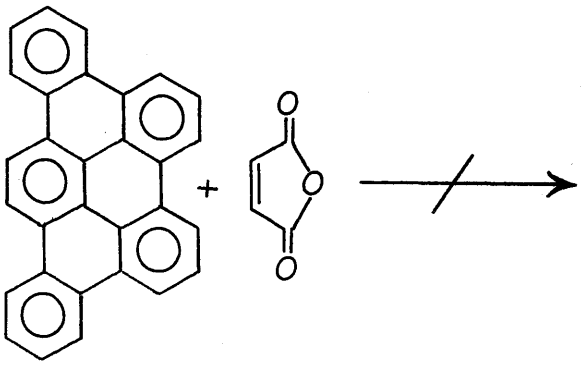


IV VI

FIGURE XI.

Comparison of the β-bands of fully benzenoid hydrocarbons.

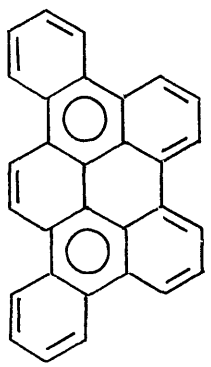
Hydrocarbon	Number of benzenoid rings	Position		Shift	
		$\overset{o}{A}$	$\sqrt{\overset{o}{A}}$	$\overset{o}{A}$	$\sqrt{\overset{o}{A}}$
	— 1 —	1819	42.65	161	1.85
	— 2 —	1980	44.50	590	6.20
	— 3 —	2570	50.70	280	2.69
	— 4 —	2850	53.39	150	1.38
	— 5 —	3000	54.77	285	2.55
	— 6 —	3285	57.32	277	2.47
	— 6 —	3277	57.24		



V

giving the anhydride (VI) with maleic anhydride/ chloranil while (V) does not react even after prolonged treatment.

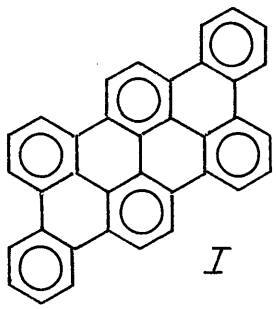
For the tribenzoperylene (V) to react in a diene synthesis would involve the sacrifice of three benzenoid rings to give (Va), and this is energetically most unfavorable.



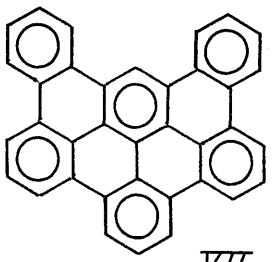
Va

Figure XI shows the increase in the wavelengths of the β-bands of the fully benzenoid series which is obtained by the successive annellation of benzenoid rings to benzene. The two isomeric tetrabenzan-

thanthrenes (I) and (VII) differ little in their wave-lengths as may be seen below:-



I



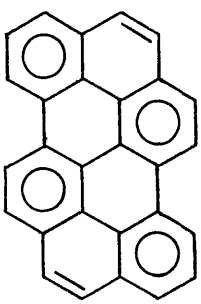
VII

λ_{β} = 3240 ⟶ 3340

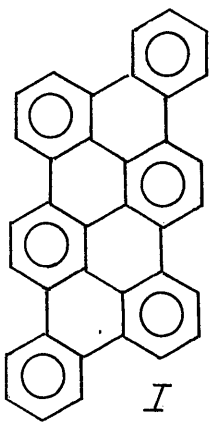
λ_{p} = 3620 ⟶ 3650

These minor spectral differences are common for isomeric hydrocarbons which have the same number of sextets. They may be termed "sextet isomers".

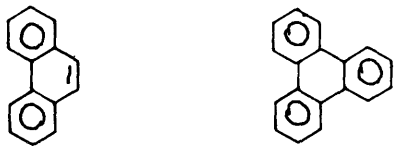
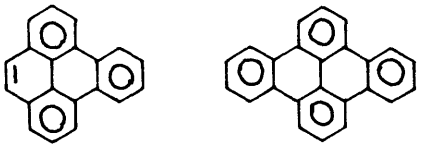
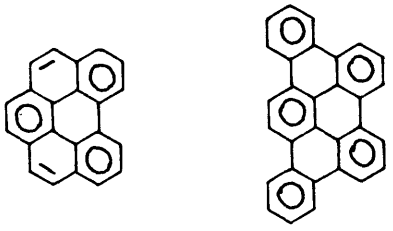
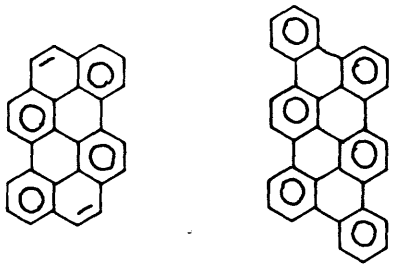
The double annellation of butadiene units to the formally fixed double bonds of the compound (VIII) to give tetrabenzanthanthrene (I) produces as expected, only a slight shift in the β-bands and p-bands.



VIII



I

Hydrocarbons	β-bands (Å)		p-bands (Å)	
	2510	2570	2925	2840
	in alcohol		in alcohol	
	2890	2850	3315	3257
	alcohol	hexane	alcohol	hexane
	3030	3000	3875	3690
	benzene	alcohol	benzene	benzene
	3245	3240	4100	4040
	dioxan	trichloro-benzene	dioxan	trichloro-benzene

Further examples are given in Table opposite. This again follows the general rule which has previously been discussed in Chapters II and III.

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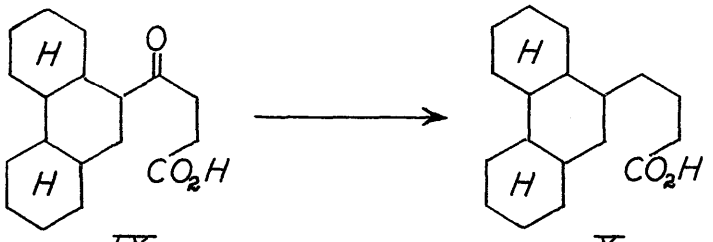
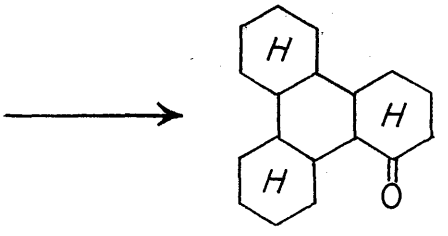
EXPERIMENTAL DISCUSSION: The first three stages of the series of reactions to be described have already been reported.(8) However, we have modified and improved all of these, and accordingly they will be given brief consideration.

1.2-3.4-5.6-7.8-Octahydrophenanthrene reacted smoothly with succinic anhydride in benzene in the

presence of aluminium chloride to give large colorless blades of β-(octahydrophenanthroyl)-propionic acid (IX). Clemmensen reduction of this keto-acid gave γ-(9-octahydrophenanthryl)-butyric acid (X) in good yield and on ring closure of this with anhydrous hydrogen fluoride, 1-keto-dodecahydrotriphenylene (XI) was obtained.



IX X



XI

This ketone was reduced with amalgamated aluminium foil and ethanol in benzene[9] to give the diol (XII) which was readily dehydrated to the hydrocarbon (XIII) on refluxing with acetic acid/acetic anhydride.

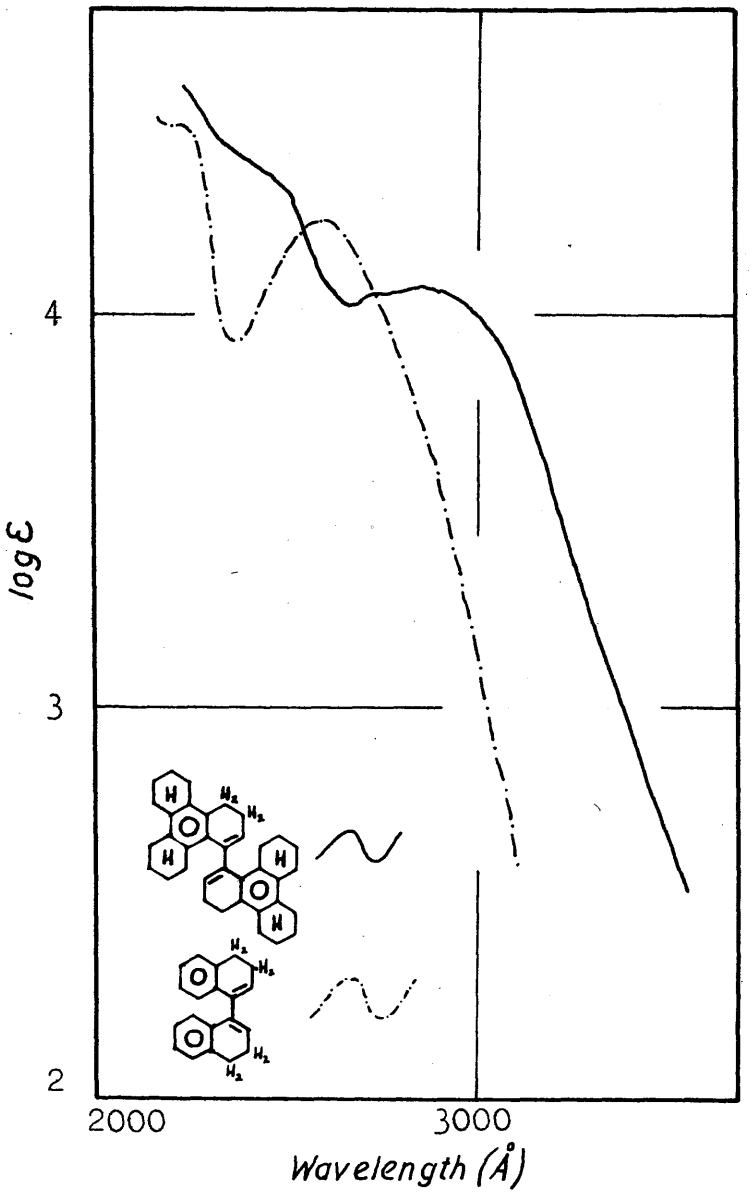
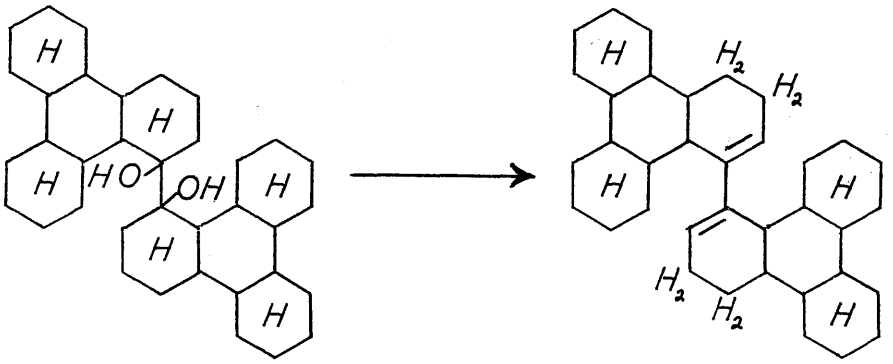


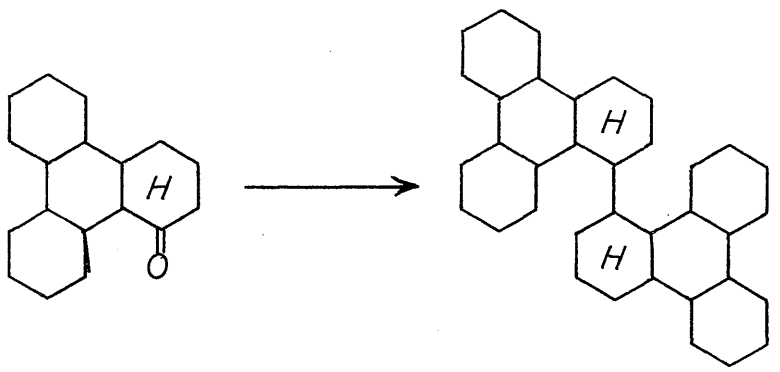
FIGURE XII. Absorption max. (Å) and log (in parentheses). 1,1'-Di-(Octahydrotriphenylenyl)(VIII) in cyclohexane, 2850 (4.07). 3,4,3',4'-Tetrahydro-1.1'-dinaphthyl in 95% ethanol, 2580 (4.24).



XII XIII

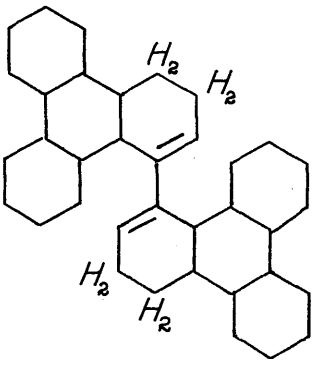
The spectrum of this dimer (XIII) is shown in Figure XII. The shift in wavelength from bis-dialin is due to the number of alkyl groups on each benzene ring.

A similar dimer was obtained by BERGMANN (10) as a by-product on Clemmensen reduction of 1.2.3.4-tetrahydrotriphenylene-1-ketone (XIV). Bergmann thought this to have the structure (XV) but by analogy with



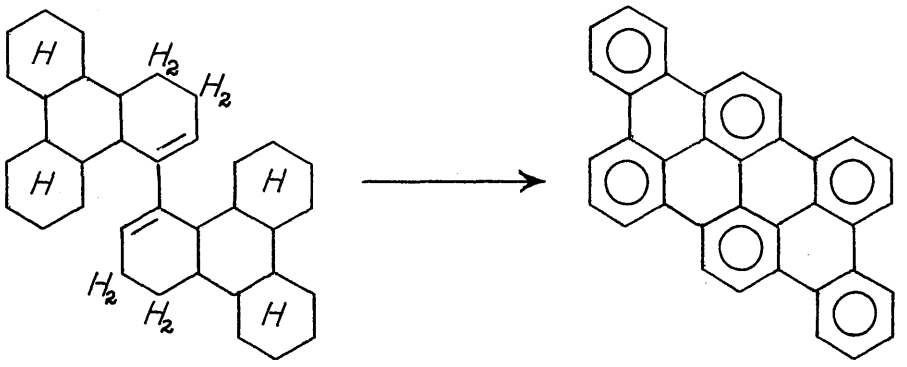
XIV XV

the present synthesis it is more probable that the structure is (XVI).



XVI

On pyrolysis under carbon dioxide with copper powder at 420°, our dimer (XIII) underwent cyclo-dehydrogenation to give tetrabenzanthanthrene (I), the absorption spectrum of which is given in Figure X.



XIII I

Although the properties, analysis, etc. of the compound make it fairly certain that cyclisation went as indicated, confirmation was sought from the infra-red spectrum. GROENWEGE[11] has shown that the

FIGURE XIII.

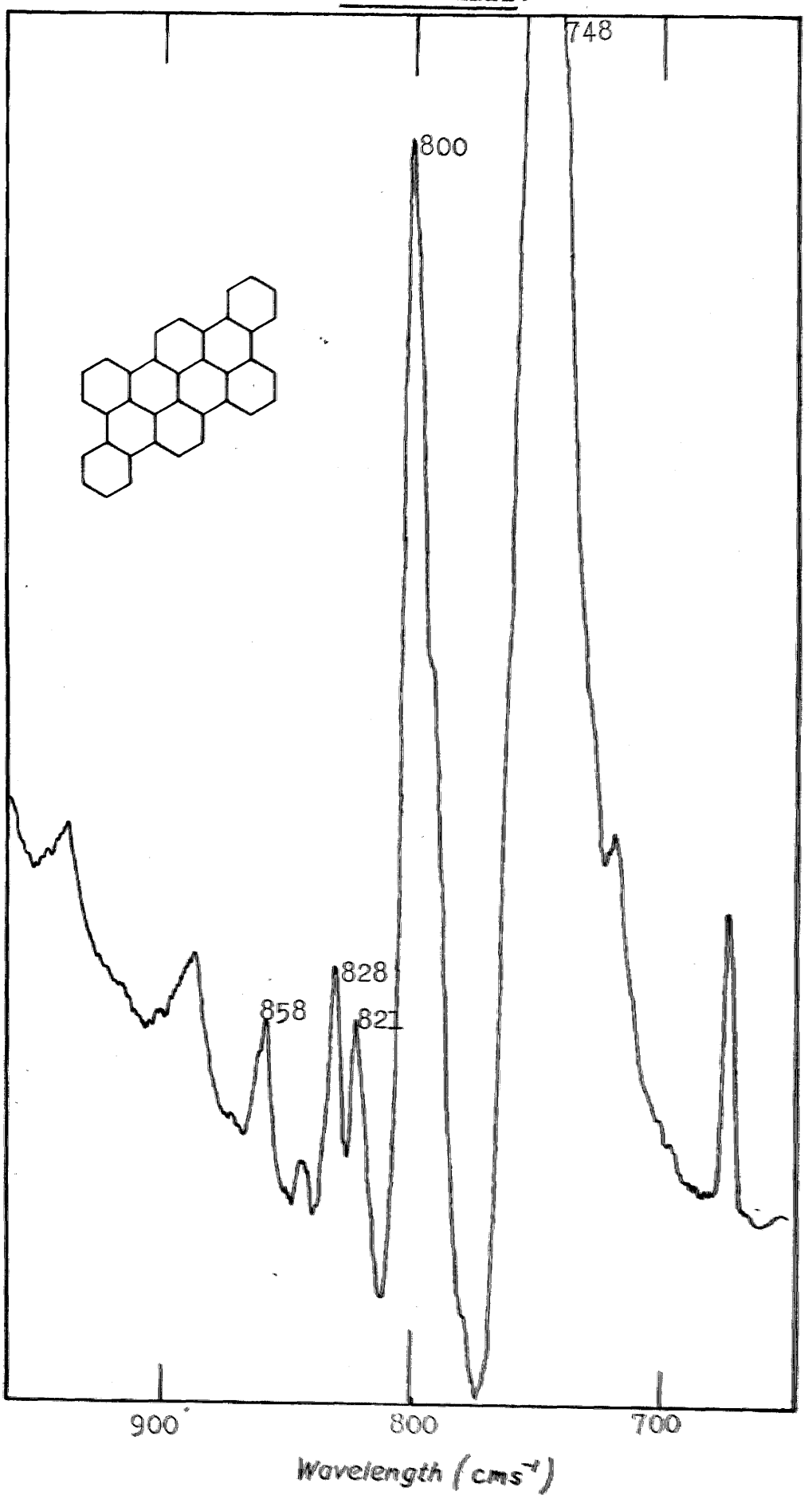
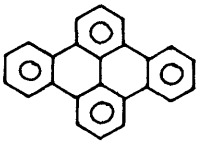
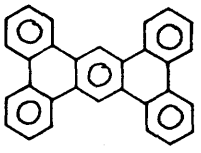
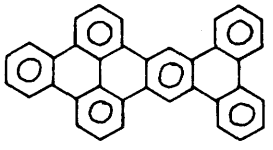
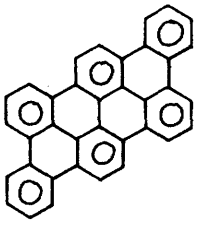


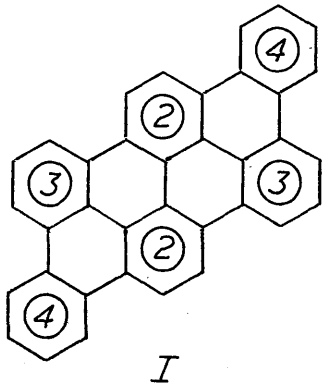
TABLE 2.

Infra-red spectra.

Hydrocarbon	C - H Vibrations (cm^{-1})			
	solo	duo	trio	quartet
	900-860	860-800	810-750	770-735
	-	-	801	744
	870	-	-	749
	871 863	-	795	746
	-	858 828 821	800	748

γ -vibrations of the C - H bonds (735-900cm^{-1}) can be used to establish the structure of polycyclic hydrocarbons. The presence of one, two, three or four hydrogen atoms on one six-membered ring gives rise to strong absorptions in the frequency ranges of 900-860 (solo), 860-800 (duo), 810-750 (trio) and 770-735cm^{-1} (quartet). ZANDER[12] has used this method to confirm the structure of tetrabenzotetracene (XVII) and CLAR and FELL[13] for tetrabenzoheptacene (XVIII).

Hence tetrabenzanthanthrene should have the structure:



I

i.e. there should be no solo absorption. The infrared spectrum of tetrabenzanthanthrene (I) is given in Figure XIII, and a comparison with some other condensed polycyclics in Table 2. This would appear to confirm the structure assigned (I).

-------oOo-------

EXPERIMENTAL.

β- 9-(1,2,3,4,5,6,7,8,-OCTAHYDROPHENANTHROYL) - PROPIONIC ACID (IX).

Powdered Aluminium chloride (40g) was added to a solution of octahydrophenanthrene (30g) and succinic anhydride (20g) in benxene (100ml). After agitation for 2½ hours at room temperature, the red mixture was decomposed with dilute hydrochloric acid and ice, and the pale green solid isolated. It was dissolved in dilute potassium hydroxide solution and the hot, filtered solution acidified to give the keto-acid (41g). It crystallised from xylene to yield large white blades (38g), m.p. 142-143° (Lit. 143-144°[8]) which dissolved in concentrated sulphuric acid to form a yellow solution.

γ - 9-(1,2,3,4,5,6,7,8-OCTAHYDROPHENANTHRYL) - BUTYRIC ACID (X).

The above acid (20g) was added to concentrated hydrochloric acid (120ml), glacial acetic acid (120ml), xylene (100ml) and zinc wool (200g). The mixture was refluxed for 6 hours, two 40ml. portions of concentrated hydrochloric acid being added during this period. The xylene layer was removed and concentrated, and the resulting colorless acid crystallised from cyclohexane. It formed white needles (14.8g), m.p. 127-128° (Lit. 128-129°[8]) and gave a yellow solution with concentrated sulphuric acid.

1-KETO-1,2,3,4,5,6,7,8,9,10,11,12-DODCEAHYDRO-TRIPHENYLENE (XI).

The above acid (10g) was added to anhydrous hydrogen fluoride (150ml), a yellow coloration developing. After 3 hours, the solution was decomposed with ice-water and the white solid obtained filtered off. This crystallised from 50% ethanol/benzene in long white needles, (7.9g), m.p. 222-223° (Lit. 222-222.5°[8]) which dissolved in concentrated sulphuric acid to give a green solution.

1,1'-DI-(3,4,5,6,7,8,9,10,11,12-OCTAHYDROTRIPHENYLENYL) (XIII).

Absolute ethanol (1oml) was added to dry benzene (120ml) and about 15ml of the resulting solution was distilled off. Freshly scratched thin aluminium foil (4g), mercuric chloride (0.6g), and finally the above ketone (12g) were added in rapid succession. The mixture was refluxed for 24 hours and the supernatent liquid decanted from the metal. On cooling, the solution deposited crystals of unreacted ketone and these were filtered off and the solvents removed. The white residue was refluxed for 3 hours with a 1:1 mixture of acetic anhydride and acetic acid. White prismatic crystals (1.3g) precipitated from solution at the beginning of ebullition. These were recrystallised from benzene, had m.p. 236-237°C and dissolved in concentrated sulphuric acid to give a ruby-red solution.

Found: C, 91,1 ; H, 8.9

$C_{36}H_{42}$ requires: C, 91.3 ; H, 8.9%

1,12:2,3:6,7:8,9-TETRABENZANTHANTHRENE (I).

The above hydrocarbon (XIII) was dehydrogenated with copper powder under carbon dioxide at 420° for 70 minutes. Sublimation of the mixture at 400° and 10^{-2} mm yielded yellow plates (15mg). These were extracted with boiling trichlorobenzene and the residue resublimed. The pale yellow plates, m.p. 530°, did not dissolve in concentrated sulphuric acid and showed an orange phosphorescence of very long life in solid solution in 1.244-trichlorobenzene, cooled in liquid air.

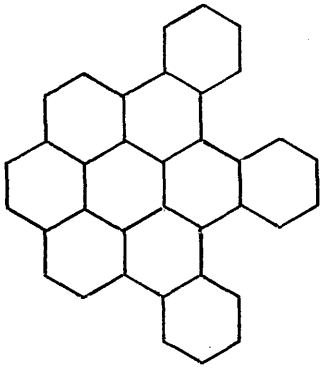
Found: C, 95.7 ; H, 4.2

$C_{36}H_{18}$ requires: C, 96.0 ; H, 4.0%

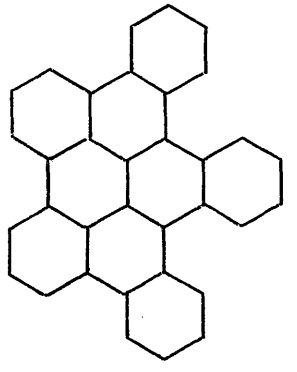
--------oOo--------

C H A P T E R V.

1.2-3.4-5.6-TRIBENZOCORONENE and 1.12-o-PHENYLENE-[2.3-10.11]-DIBENZOPERYLENE.

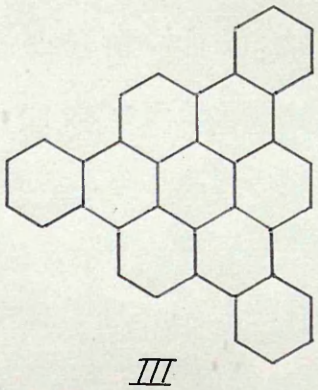


I



II

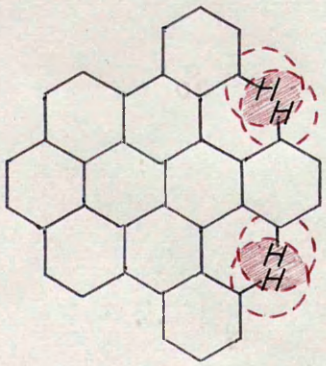
INTRODUCTION: 1.2-3.4-5.6-Tribenzocoronene (I) was synthesised for spectral comparison with the fully benzenoid 1.2-5.6-9.10-tribenzocoronene (III). However, attempts to prepare this latter were unsuccessful (vide Appendix I).



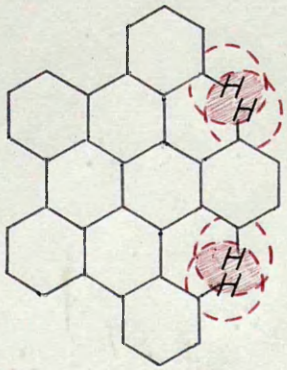
III

1.12-o-Phenylene-[2.3-10.11]-dibenzoperylene (II) was also prepared by a method very similar to that of (I).

THEORETICAL DISCUSSION: Consideration of the structures of both tribenzocorone (I) and o-phenylene-dibenzoperylene (II) makes it clear that there is considerable steric overcrowding in the molecules.

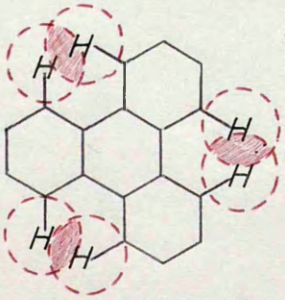


Ia

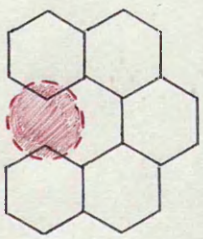


IIa

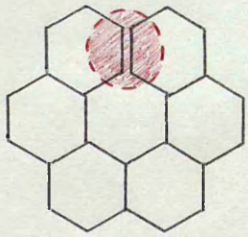
Obviously these molecules cannot be uniplanar but must be slightly twisted in order to accomodate the hydrogen atoms marked in (Ia) and (IIa). The chemistry of both tribenzocoronene and o-phenylene-dibenzoperylene is then fundamentally the chemistry possessed by these sterically overcrowded molecules. Reference has already been made (Chapter I) to the steric inhibition caused by the hydrogen atoms in triphenylene (IV) and phenanthrene. Other molecules exhibit even stronger intramolecular overcrowding effects. Among these may be mentioned dibenzophenanthrene (VI)[1] and hexahelicene (VII)[2].



IV



VI

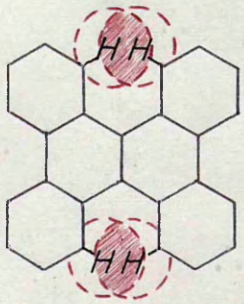


VII

This latter hydrocarbon - so called because of its helical shape - is probably the classic example of intramolecular overcrowding. It has been resolved into its stereo-isomers.[2]

These overcrowded molecules have, in general, rather indistinct melting points and their solubilities are somewhat higher than a consideration of their molecular weight would suggest. These facts are readily explicable in terms of the racemic mixtures of which they are composed.

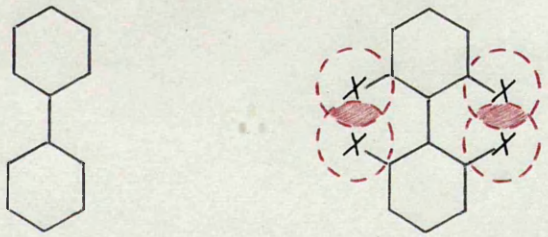
The absorption spectra of molecules exhibiting intramolecular overcrowding must here be mentioned. These spectra tend to be rather diffuse and more strongly shifted to the red than would be expected from the predictions of the annellation principle. Thus in tetrabenzonaphthalene (VIII), the β-band $_{o(3)}$ must be corrected by a value as large as -140A.



VIII

The explanation for this is that the molecules are twisted from the plane and since interaction or delocalisation requires the molecule to be uniplanar, this naturally causes considerable differences of spectra. This may be demonstrated in the case of diphenyl (IX) which has been shown to have some double

bond character in the 1'.1'-bond.[4] However, when bulky substituents are present in the 2- and 2'-positions the two benzene rings cannot attain planarity and hence there can be no conjugation character in the central bond. The consequent restriction of rotation about the central bond is manifest in the spectra of compounds of this type:



IX

Before further study of spectra is possible, it will be necessary to consider the electronic transitions underlying the spectra of aromatic hydrocarbons in general.[5]

The various electronic transitions (α, β - and p-) may be represented by equations of the type:

$$\nu = \frac{R}{K^2}$$

where ν is the frequency of the transition, R is the Rydberg Constant and K is a variable constant (Order Number) which increases by a constant amount for the annellation of rings, and which is a simple function of the number of π-electrons.

The α-bands of an aromatic hydrocarbon are represented by the equation:

$$\nu_\alpha = \frac{12^2 R}{K^2}\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$\text{or} \quad \lambda_\alpha = \frac{K^2}{20R}$$

------while the β-bands may be represented by:

$$\nu_\beta = \frac{12^2 R}{K^2}\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$\text{or} \quad \lambda_\beta = \frac{K^2}{27R}$$

It may be seen that the frequencies ν_α and ν_β are in the ratio:

$$\nu_\alpha : \nu_\beta = \left(\frac{1}{2^2} - \frac{1}{3^2}\right) : \left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$= \underline{\underline{1 : 1.35}}$$

$$\text{or } \lambda_\alpha : \lambda_\beta = \frac{K^2}{20R} : \frac{K^2}{27R}$$

$$= \underline{\underline{1.35 : 1}}$$

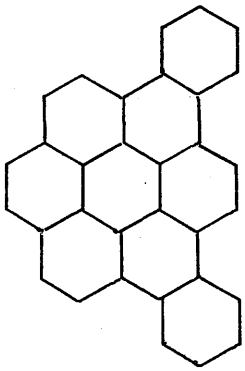
Thus in any aromatic hydrocarbon the wavelength of the α-band should be 1.35 times that of the β-band. This ratio is observed experimentally.

In non-planar molecules, however, this ratio decreases by amounts depending upon the deformation present in the molecule.

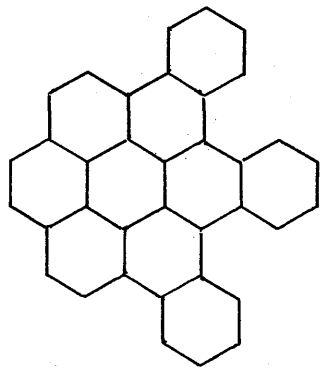
Typical values are as follows:

HYDROCARBON	α/β
Triphenylene [6]	1 : 1.30
1.2-7.8-Dibenzonaphthalene [7]	1 : 1.32
1.2-5.6-7.8-11.12-Tetra-benzocoronene [8]	1 : 1.29
1.2-3.4-5.6-7.8-Tetra-benzo-naphthalene [3]	1 : 1.25
1.2-3.4-5.6-Tribenzocoron-ene (I)	1 : 1.31
1.12-o-Phenylene- 2.3-10.11 - dibenzoperylene (II)	1 : 1.31

The following shifts in the wavelengths of the β-bands are observed in passing from 1.2-5.6-dibenzocoronene (X) [9] to 1.2-3.4-5.6-tribenzocoronene (I) and from 1.12-2.3-10.11-tribenzoperylene (XI) [10] to 1.12-o-phenylene- 2.3-10.11 -dibenzoperylene (II):

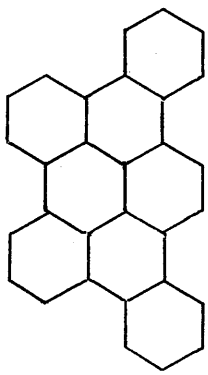


X

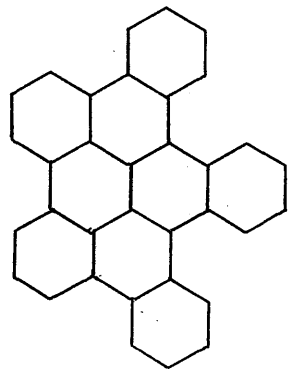


I

λ_β = 3280 $\xrightarrow{+260}$ 3540 Å



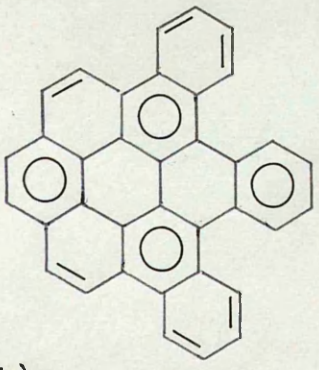
XI



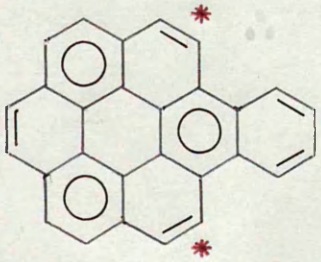
II

λ_β = 3000 $\xrightarrow{+260}$ 3260 Å

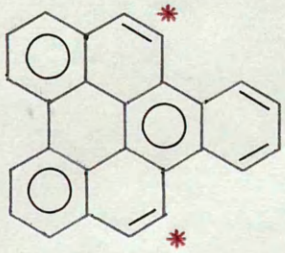
These shifts are much as expected for the annellation of butadiene units in the acene series, and it is obvious that in neither case is there a new benzenoid ring formed as there would be in a situation such as:



If benzocoronene (11) exists exclusively in the form (XII) and o-phenylene-perylene (12) in the form (XIII), it is obvious that the annellation of butadiene to the formally fixed double bonds marked (*), should produce little change in the wavelength of the β-bands.

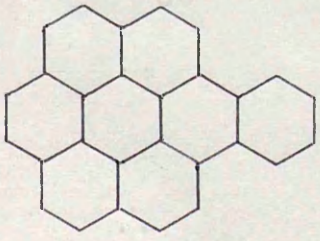


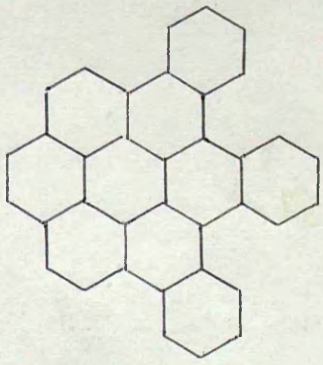
XII



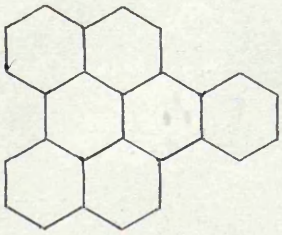
XIII

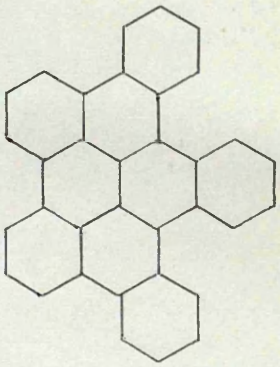
However, the shifts are as follows:





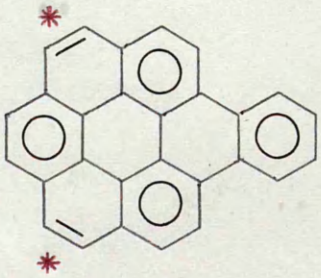
λ_β = 3200 $\xrightarrow{+340}$ 3540 Å





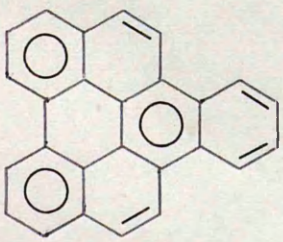
λ_β = 3105 $\xrightarrow{+155}$ 3260 Å

The differences in these two shifts are presumably caused by the fact that benzocoronene would be rather expected to exist in the form (XIIa) in which the double bonds are fixed in the 5.6 and 9.10 positions.

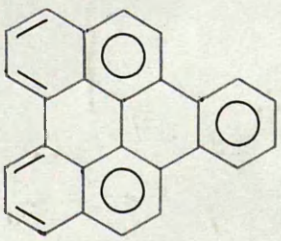


XIIa

o-Phenylene-perylene on the other hand can exist in either of the forms (XIIIa) or (XIIIb).

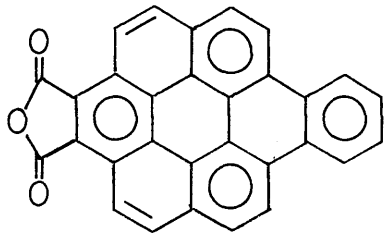


XIIIa



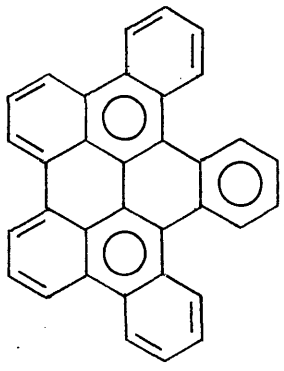
XIIIb

These have equal energy and hence either might be expected. The rather low shift in the β-band indicates that the 2.3 and 10.11 bonds must have considerable double bond character. The existence of the molecule in the second form (XIIIb) manifests itself in the reaction with maleic anhydride/chloranil to give the anhydride (XIV).[13]



XIV

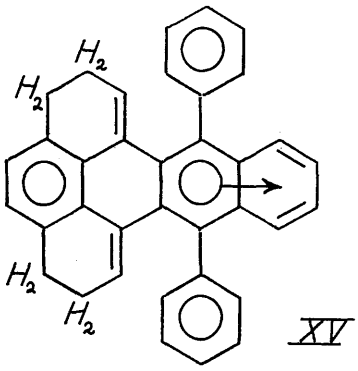
1.12-o-Phenylene-[2.3-10.11]-dibenzoperylene (II) does not react with maleic anhydride/chloranil even after an extended reaction time. This is probably due to the fact that for the molecule to assume the form (IIa)



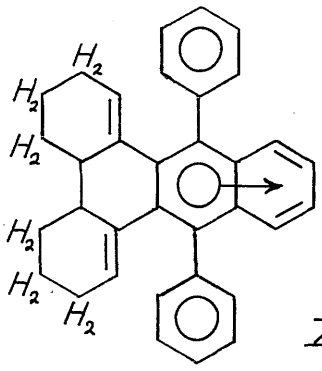
IIa

would involve the sacrifice of two benzenoid rings and this is energetically unlikely.

In the course of these syntheses, the two compounds (XV) and (XVI) were obtained.

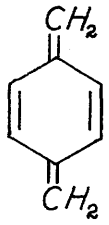


XV



XVI

These are known as quino-dimethides. While they are related to p-xylylene (XVII), this latter polymerises



XVII

very readily whereas these compounds are quite stable. This type of skeleton is somewhat unusual, and it may be that the splitting of conjugation in the central acene unit confers enhanced stability on the molecules. Thus in (XV) it is apparent that there is no tetracene unit present. This is possibly related to

the work done by CLAR on methyl acenes.[14] It was shown that on ascending the acene series, the isomeric methylene-dihydroacenes become predominant.

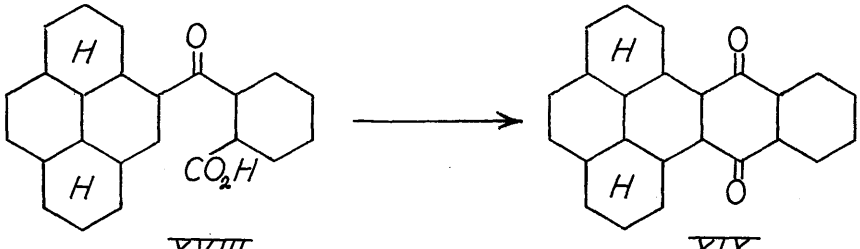
-------oOo-------

EXPERIMENTAL DISCUSSION: Although the syntheses of these hydrocarbons (I) and (II) were very similar, it will be more convenient to treat each separately since

the course of the reactions involved were not always identical:-

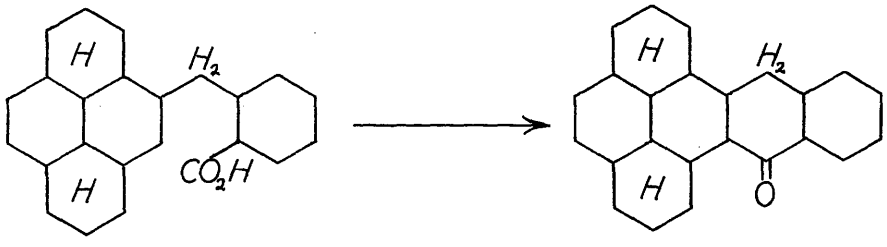
(a) 1.2-3.4-5.6-Tribenzocoronene.

The reaction of hexahydropyrene with phthalic anhydride in the presence of aluminium chloride gave 1-o-carboxybenzoylhexahydropyrene (XVIII) in good yield.(15)(16) The cyclisation of this keto-acid to the quinone (XIX) was accomplished with anhydrous hydrogen fluoride.



XVIII XIX

It is of interest to note that CAMERON and COOK(15) were unable to directly ring-close this acid with various other reagents but were compelled first to reduce the carbonyl group -



XX

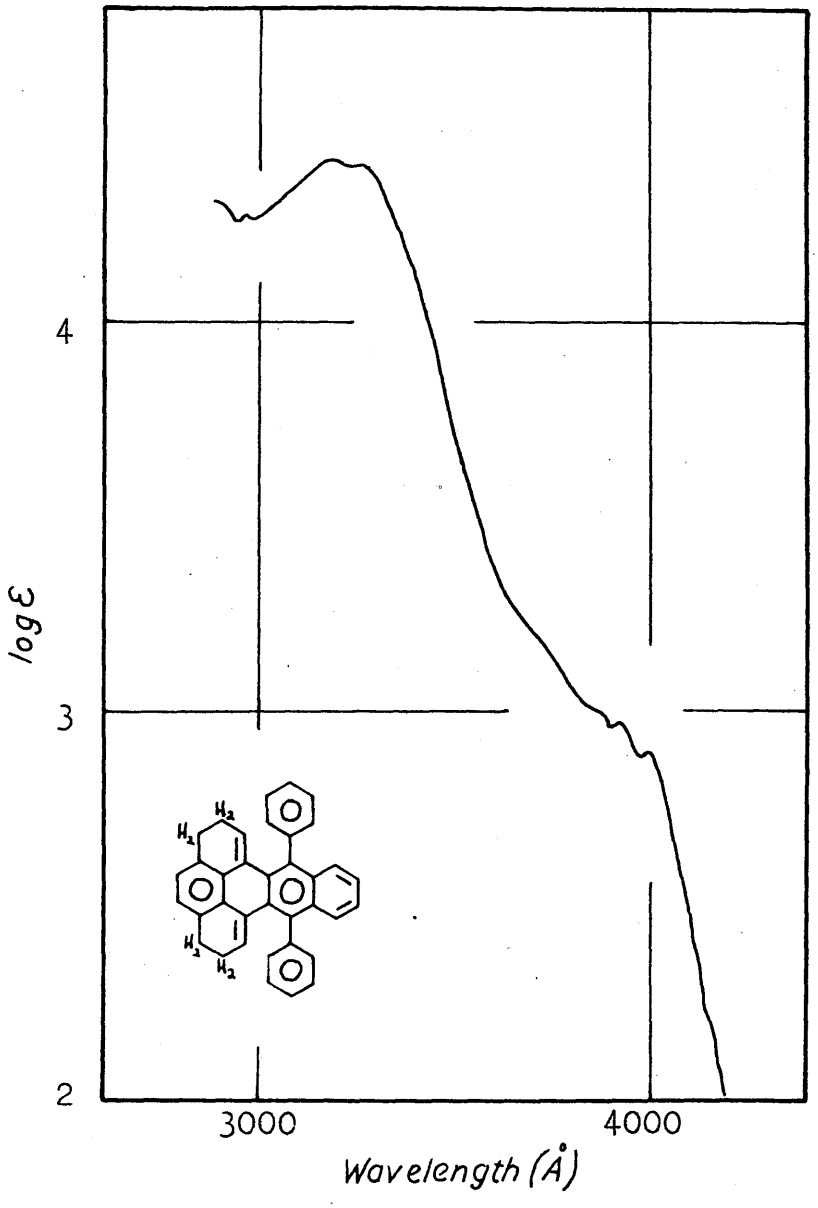
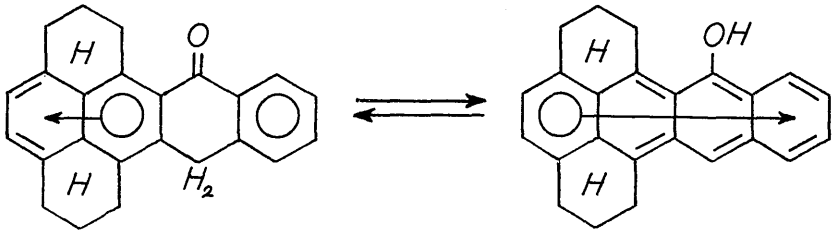


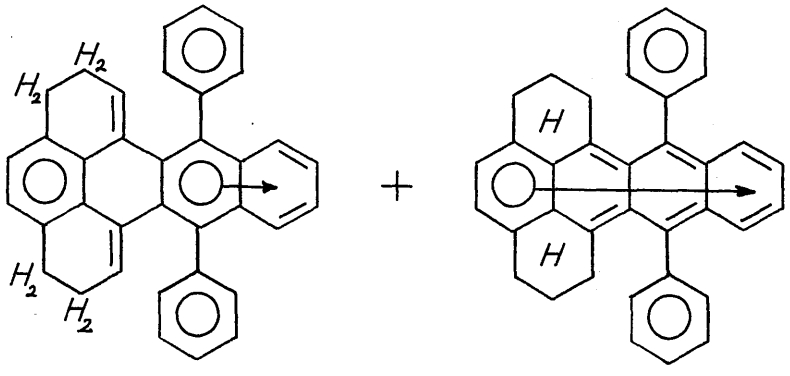
FIGURE XIV. Absorption max. (Å) and log (in parentheses). Quinodimethide (XV) derived from naphthopyrene in benzene, 3190 (4.41).

These authors also reported that the anthrone (XX) resulting from cyclisation did not react with phenyl magnesium bromide. This may be ascribed to the ready enolization of compounds of this type:



XX

In the present case, the reaction of the quinone (XIX) with phenyl lithium was found to be quite vigorous, and two compounds were obtained from the reaction. One of these is the quino-dimethide (XV), the spectrum of which is given in Figure XIV, and the other, a red compound, the diphenyl naphthopyrene derivative (XXI):



XV XXI

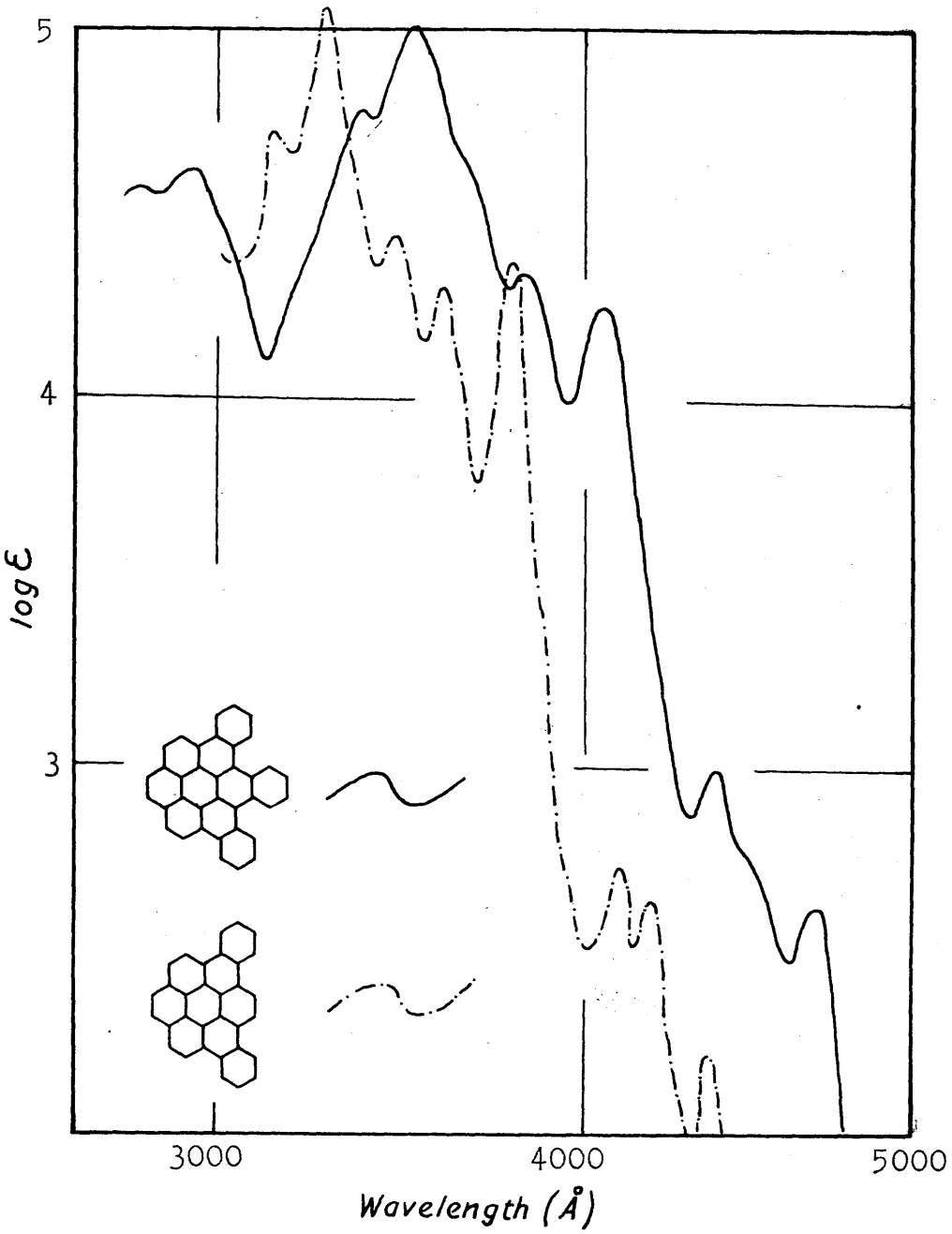
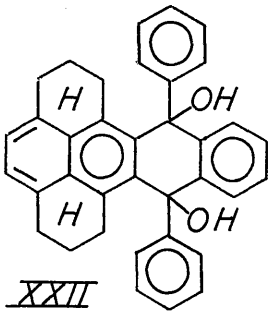


FIGURE XV. Absorption max. (Å) and logε (in parentheses). 1.2-3.4-5.6-Tribenzocoronene (I) in benzene. α : 4630 (2.61), 4360 (3.00); p : 4050 (4.26), 3840 (4.35); β: 3540 (5.01), 3390 (4.78); β': 2930 (4.62). 1.2-5.6-Dibenzocoronene in trichlorobenzene, α : 4335 (2.25), 4180 (2.66), 4100 (2.75); p : 3790 (4.38), 3600 (4.31), 3490 (4.55); β : 3280 (5.06), 3140 (4.72).

It is obvious that the intermediate diol (XXII) must be extremely labile and must split out the elements

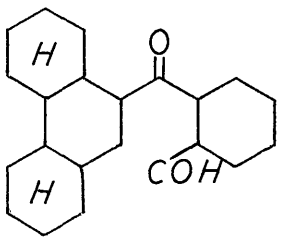


XXII ⟶ XV + XXI

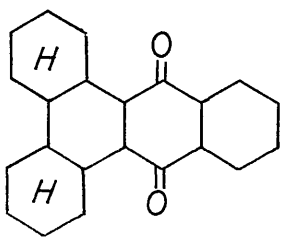
of water under the conditions of the reaction to form the compounds (XV) and (XXI). Both these compounds (XV) and (XXI) give tribenzocoronene (I) on pyrolysis with copper powder at 410°.
The spectrum of tribenzocoronene (I) is shown in Figure XV.

(b) 1.12-o-Phenylene- 2.3-10.11 -dibenzoperylene.

Octahydrophenanthrene reacted smoothly with phthalic anhydride in a Friedel-Crafts reaction to give 1-o-carboxybenzoyl-octahydrophenanthrene (XXIII).(17) This cyclised smoothly to the quinone (XXIV) with anhydrous hydrogen fluoride.



XXIII ⟶



XXIV

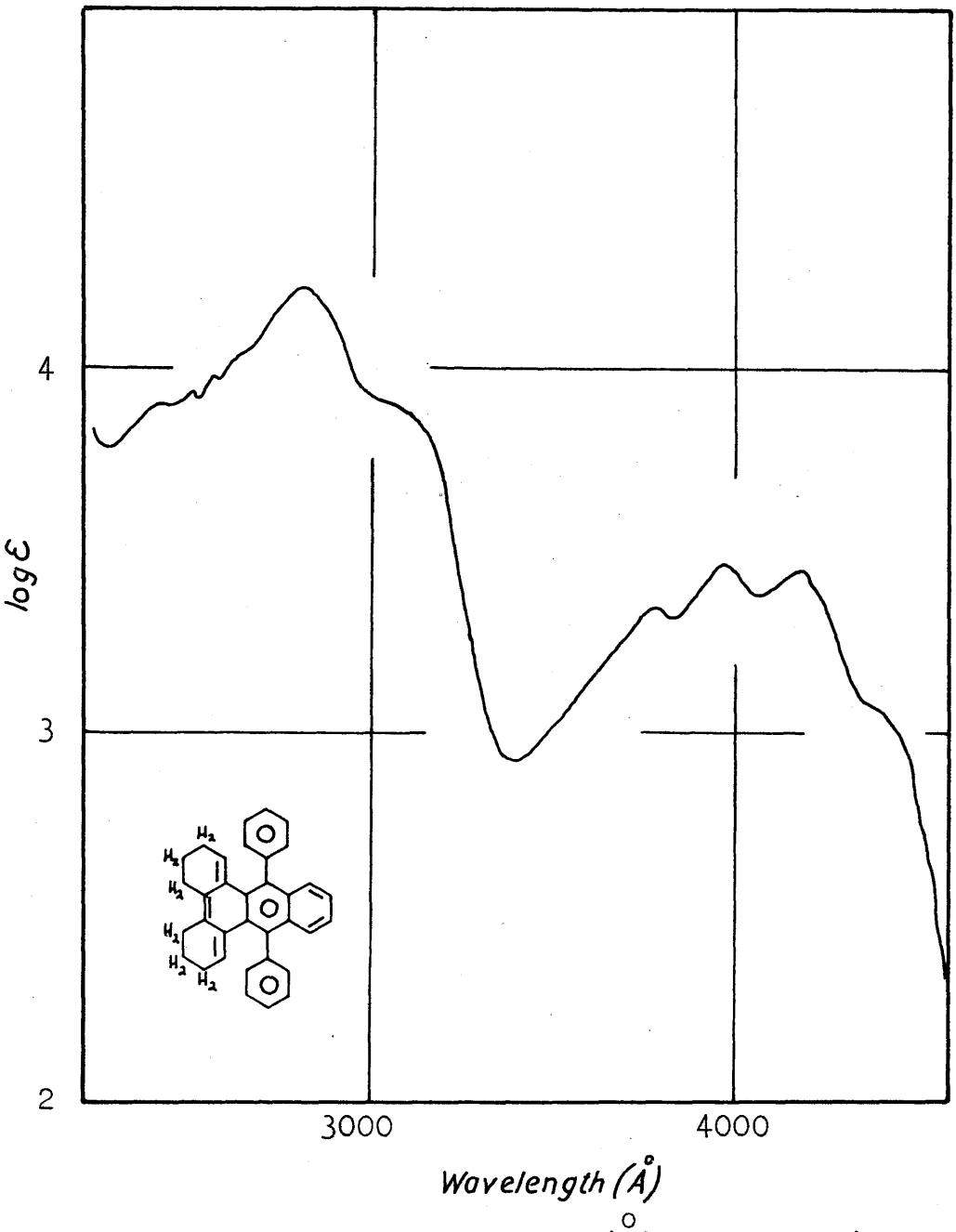


FIGURE XVI. Absorption max. (Å) and log (in parentheses). Quinodimethide (XVI) derived from dibenzanthracene in cyclohexane, 2820 (4.22), 3080 (3.90), 3670 (3.34), 3970 (3.46), 4180 (4.44).

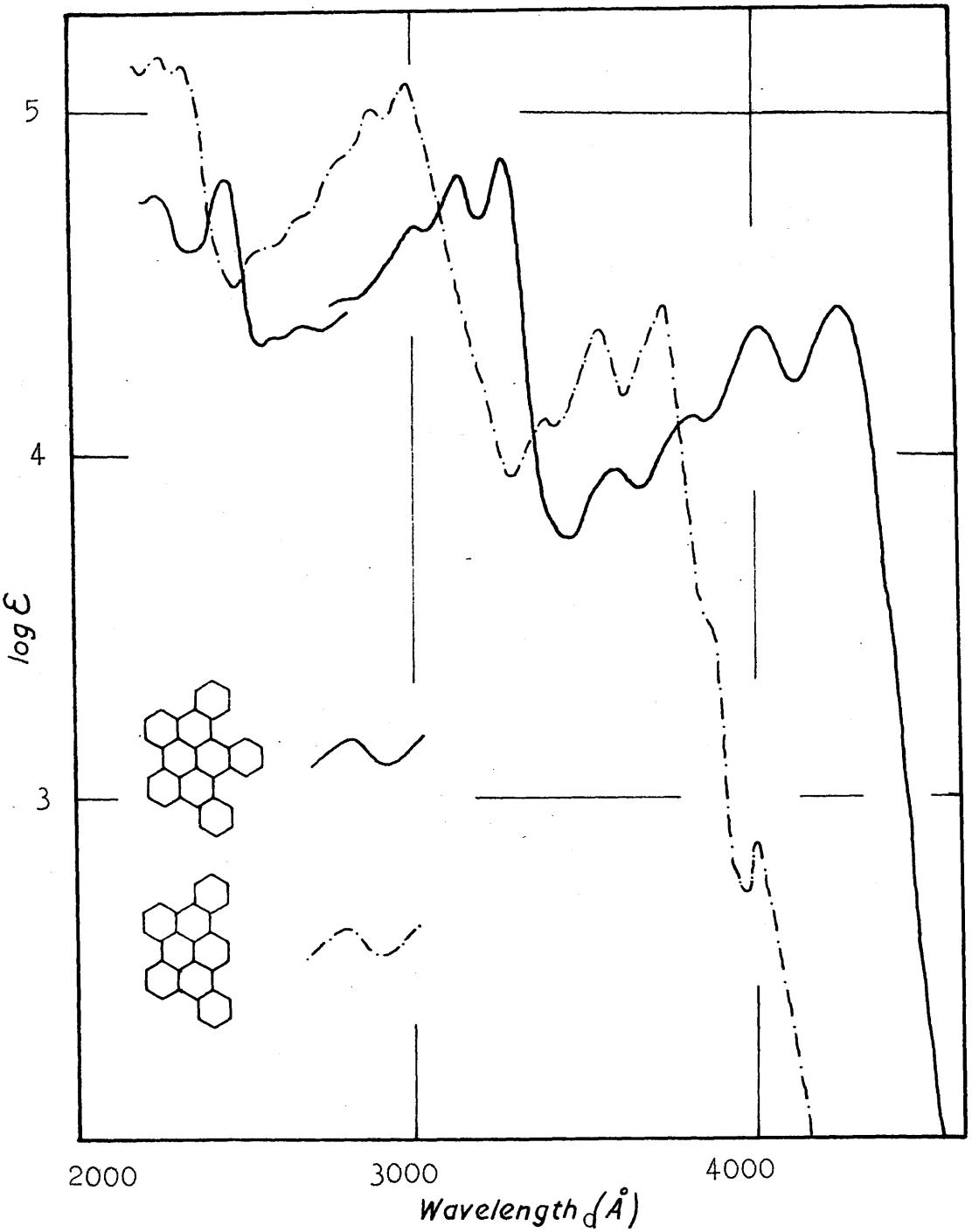
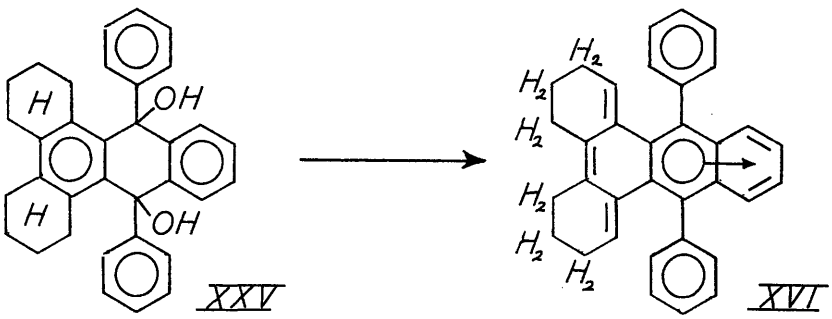


FIGURE XVII. Absorption max. (A) and log (in parentheses). 1.12-o-Phenylene-2.3-10.11-Dibenzoperylene (II) in benzene, p : 4250 (4.43), 4010 (4.37), 3820 (4.11), 3580 (3.96); β: 3270 (4.87), 3140 (4.82), 3010 (4.67); β′: 2450 (8.41). From 2800A in cyclohexane.
1.12-2.3-10.11-Tribenzoperylene in trichlorobenzene, α : 4010 (2.86); p : 3740 (4.45), 3540 (4.37), 3380 (4.11); β : 3000 (5.09), 2880 (5.00); β′: 2340 (5.14). From 3000A in ethanol.

The quinone (XXIV) on treatment with phenyl lithium gave the diol (XXV), which was readily dehydrated to give the quino-dimethide (XVI), the spectrum of which is shown in Figure XVI. It is obvious that the compound is contaminated with a little phenylene dibenzoperylene (II), which is possibly formed by spontaneous cyclo-dehydrogenation.



Both the diol and the quino-dimethide gave 1.12-o-phenylene- 2.3-10.11 -dibenzoperylene on pyrolysis with copper powder at 410°, and the absorption spectrum of this is shown in Figure XVII.

-------oOo-------

E X P E R I M E N T A L.

1-o-CARBOXYBENZOYL-HEXAHYDROPYRENE (XVIII).

Aluminium chloride (35g) was added to a mixture of hexahydropyrene (20g) and phthalic anhydride (15g) in benzene (60ml). The color immediately became red-brown going to claret and much hydrogen chloride was evolved. After agitation for 2 hours at room temperature, the mixture was decomposed with dilute hydrochloric acid and ice, and after the benzene had been removed by steam distillation, a beige resin was obtained. This was dissolved in dilute sodium hydroxide solution and the hot filtered solution acidified with hydrochloric acid. The resulting beige material crystallised from xylene as colorless needles of

1-o-carboxybenzoyl-hexahydropyrene, (45g), m.p. 179-181°, (Lit. 176.5-178° [15]). It dissolved in concentrated sulphuric acid to give the following color series: violet - brown - yellow - green.

NAPHTHO-[2'.3'-1.2]-HEXAHYDROPYRENE-1'.4'-QUINONE (XIX).

The above keto-acid (5g) dissolved in anhydrous hydrogen fluoride (100ml) to give a violet coloration which rapidly became green. This was left at room temperature for 20 hours, decomposed with ice-water and the yellow solid filtered off. Crystallisation from xylene gave bright yellow needles (3.9g) of the quinone, m.p. 197-198°, which dissolved in concentrated sulphuric acid to give a blue green solution. It did not form a vat with alkaline sodium dithionite.

Found: C, 85.1 ; H, 5.7

$C_{24}H_{18}O_2$ requires: C, 85.2 ; H, 5.4%

TREATMENT OF THE ABOVE QUINONE WITH PHENYL LITHIUM.

A solution of the quinone (2g) in dry benzene (30ml) was added to an ethereal solution of phenyl lithium (prepared from bromobenzene (3g) and lithium

(0.4g)), the color immediately becoming red. The ether was distilled off and the solution was refluxed for 15 minutes. The solution was permitted to cool and then poured into acetic acid/ice water. The red material obtained after the removal of the benzene by steam distillation was thoroughly extracted with ether and the pale pink material remaining (0.4g) crystallised from benzene as white needles of 1'.4'-diphenyl- 4.5.8.9 -tetrahydronaphtho- 2'.3'-1.2 - pyrene (XV), m.p. 312-314°. These gave a green coloration with concentrated sulphuric acid.

Found: C, 94.5 ; H, 5.4

$C_{36}H_{26}$ requires: C, 94.3 ; H, 5.7%

The red solid obtained by evaporation of the ether extracts proved to be the diphenyl-tetracene derivative (XXI).

Found: C, 94.0 ; H, 6.1

$C_{36}H_{28}$ requires: C, 93.9 ; H, 6.1%

This photo-oxidised very rapidly.

1.2-3.4-5.6-TRIBENZOCORONENE (I).

The crude red material (1g) was ground with copper powder and pyrolysed under carbon dioxide at

420° for 1 hour. The copper was then thoroughly extracted with benzene, the resulting solution chromatographed on grade "O" alumina and the red solution obtained, concentrated to give a dark yellow solid. This was sublimed at 330° and 10^{-2} mm and the red oil obtained crystallised from benzene as yellow needles (0.15g), m.p. 350-351°. These were insoluble in concentrated sulphuric acid.

Found: C, 95.9 ; H, 4.3

$C_{36}H_{18}$ requires: C, 96.0 ; H, 4.0%

9-o-CARBOXYBENZOYLOCTAHYDROPHENANTHRENE (XXIII).

Octahydrophenanthrene (30g) and phthalic anhydride (25g) were dissolved in benzene (70ml) and aluminium chloride (35g) added. The color of the solution became orange-yellow, quickly going to yellow-red and there was a vigorous evolution of hydrogen chloride. After agitation for 2½ hours at room temperature, the mixture was decomposed with dilute hydrochloric acid and the benzene removed by steam distillation. The resulting grey material was dissolved in dilute potassium hydroxide and the hot, filtered solution treated with hydrochloric acid, an

ivory solid being obtained. This crystallised from xylene as colorless needles of 9-o-carboxybenzoyl-octahydrophenanthrene, (42g), m.p. 201-202° (Lit. 200°)[17] which dissolved in concentrated sulphuric acid to give a red solution.

NAPHTHO- 2'.3'-9.10 -OCTAHYDROPHENANTHRENE-1'.4'-QUINONE (XXIV).

The above keto-acid (10g) was slowly added to anhydrous hydrogen fluoride (200ml), the color darkening rapidly from the original yellow to yellow-brown. After 18 hours, the solution was decomposed with ice-water and the pale yellow solid obtained extracted with dilute sodium carbonate. The yellow material remaining (5g) crystallised from xylene as long pale yellow rods of naphtho-octahydrophenanthrene quinone, m.p. 242-244° (Lit. 238-239°[18] or 234-235°[19]) which gave a ruby red solution in concentrated sulphuric acid.

Acidification of the carbonate solution with dilute hydrochloric acid gave the unreacted keto-acid (4.2g).

9.10-DIPHENYL-9.10-DIHYDROXY- 1'.2'.3'.4'.1".2".3".4" - OCTAHYDRO-1.2-3.4-DIBENZ-ANTHRACENE.

A solution of the quinone (XXVI) (3g) in dry benzene (50ml) was slowly added to an ethereal solution of phenyl lithium (prepared from 4g bromobenzene and 0.4g lithium). There was little color change initially, but after the removal of the ether the color became brown with a green fluorescence. The solution was refluxed for 2 hours, cooled and poured into ice-water. The benzene was removed and the orange solid obtained was washed with dilute acetic acid and thoroughly extracted with ether. On filtration, a white insoluble material (2.5g) was obtained. This crystallised from benzene as a white solid, m.p. 260-264° (decomp.) which dissolved in concentrated sulphuric acid to give a green going to brown solution, with a maroon fluorescence.

Found: C, 86.50 ; H, 6.69

$C_{34}H_{32}O_2$ requires: C, 86.40 ; H, 6.77%

DEHYDRATION OF DIOL.

The diol (1g) was dissolved in glacial acetic acid and one drop of concentrated hydrochloric acid added. The solution immediately became yellow and on refluxing for 10 minutes a yellow solid precipitated out. This was filtered off and crystallised from benzene as greenish-yellow needles, m.p. 281-282°. With concentrated sulphuric acid the material gave first a pink solution, but this became red with a red fluorescence on standing.

Found: C, 93.8 ; H, 5.9

$C_{34}H_{28}$ requires: C, 93.9 ; H, 6.1%

1.12-o-PHENYLENE- 2.3-10.11 -DIBENZOPERYLENE (II).

The diol (2g) was ground with copper powder and pyrolysed under the protection of a stream of carbon dioxide at 400° for 30 minutes. A yellow oil sublimed in the tube, and this and the copper powder were extracted with benzene, and the solution chromatographed over alumina. Concentration of the yellow solution gave a yellow solid which sublimed as a yellow oil. This crystallised from benzene as yellow ferns of benzoanthrene, (0.7g), m.p. 324-324.5° and gave very

slowly a blue solution with concentrated sulphuric acid.

Found: C, 95.7 ; H, 4.4

$C_{34}H_{18}$ requires: C, 95.8 ; H, 4.3%

The solution in benzene has a strong blue fluorescence.

An attempt was made to obtain the maleic anhydride adduct of the hydrocarbon by refluxing it with maleic anhydride and chloranil for 5 hours. However, no evidence for reaction could be obtained.

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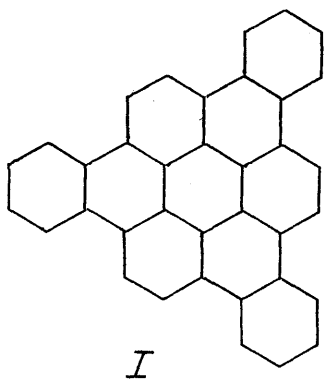
A P P E N D I X I.

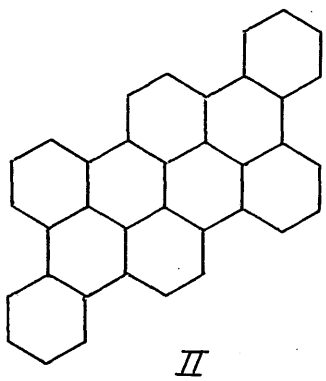
ATTEMPTED SYNTHESES OF 1.2-5.6-9.10-TRIBENZOCORONENE.



I

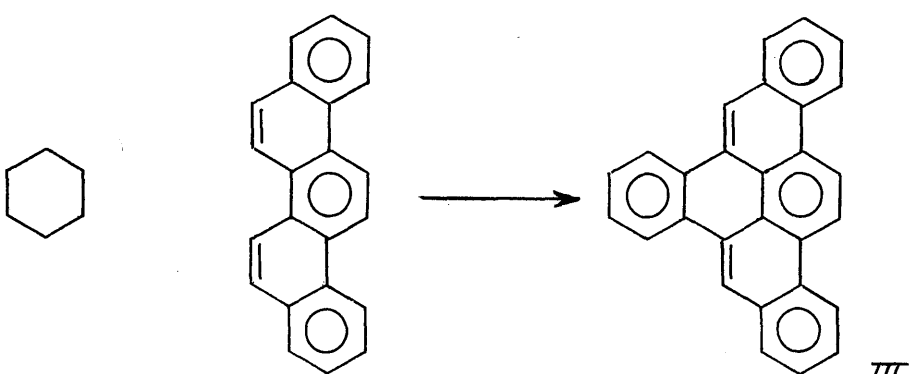
INTRODUCTION: Attempts were made to prepare 1.2-5.6-9.10-tribenzocoronene (I). This hydrocarbon has considerable theoretical interest as it would be fully benzenoid and hence would be expected to possess the characteristic properties of these compounds. In addition to this, it would possess trigonal symmetry and would

also be comparable with the isomeric tetrabenzanthanthrene (II):



II

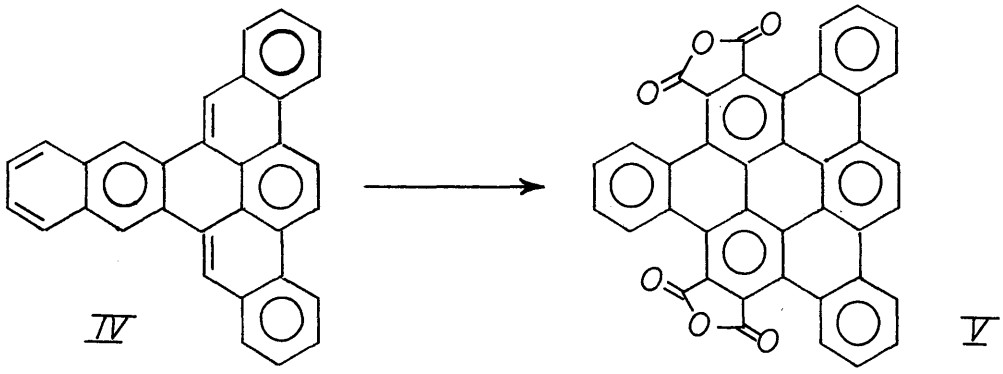
EXPERIMENTAL DISCUSSION: The preparation of 1:2-4:5-8:9-Tribenzopyrene (III) by the reaction of benzene with picene in the presence of aluminium



III

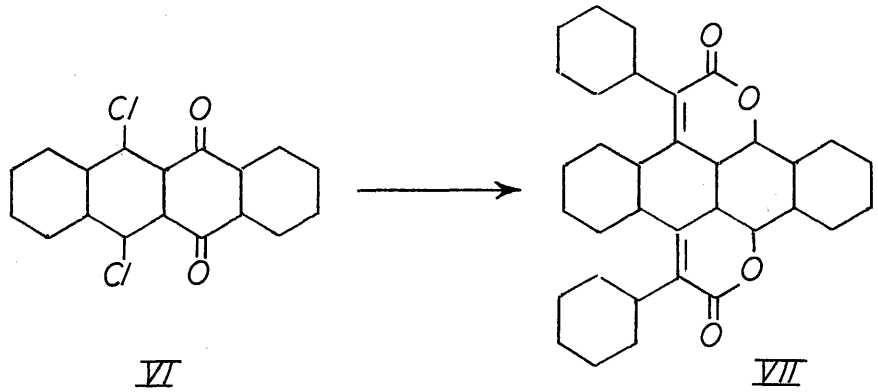
chloride has been reported.(1) Accordingly the reaction of naphthalene and picene was investigated in an attempt to obtain 1.2-naphtho-4.5-8.9-dibenzopyrene (IV) which would be expected to react with maleic anhydride in a double diene synthesis to give

tribenzocoronene dianhydride (V). Various solvents and conditions were used for the reaction but no success was achieved by this method.



IV V

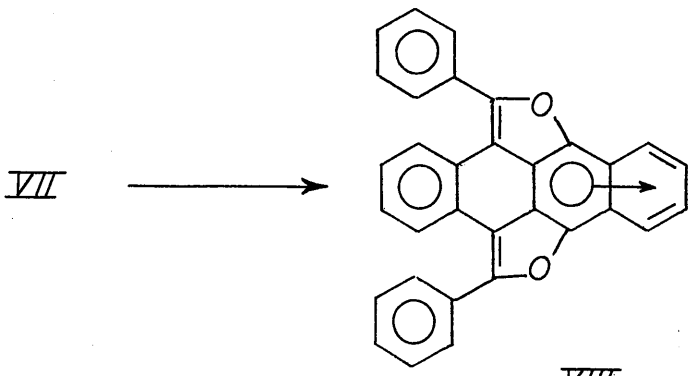
Attempts were also made to prepare 1.2-naphtho-4.5-8.9-dibenzopyrene (IV) by a condensation reaction. Benzyl cyanide reacted with 6.11-dichlorotetracene-5.12-quinone (VI) in the presence of strong alkali to give the dilactone (VII):



VI VII

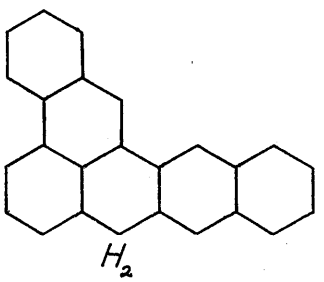
This dilactone was boiled with ethanol and strong alkali in the presence of air, and a violet-red

compound was obtained on the addition of sodium hydrosulphite. This is thought to be the dioxido-compound (VIII):

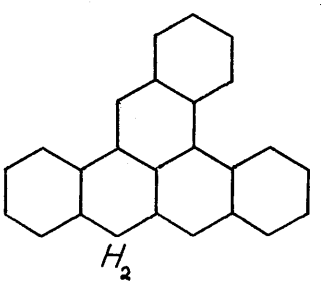


VII VIII

An aluminium chloride melt on this compound yielded mainly tetracene together with a small amount of a yellow material which is thought to be a mixture of 7.8-benzo-naphtho-[1'.3'-1.9]-anthrene (IX) and 2.3-benzo-naphtho-[1'.3'-1.9]-anthrene (X).



IX



X

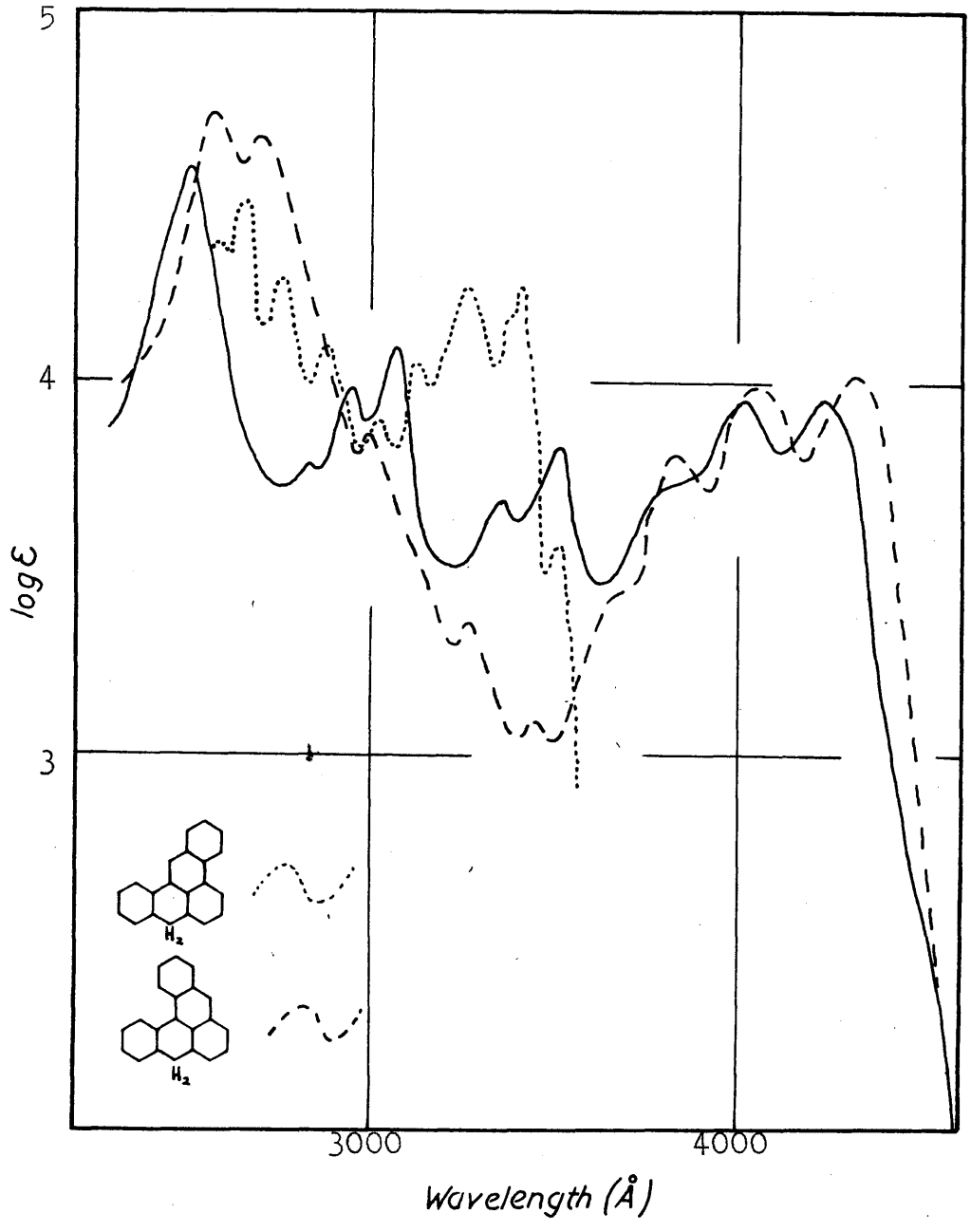


FIGURE XVIII. Absorption max. (Å)and logε (in parentheses). Product from aluminium chloride melt (IX + X) in cyclohexane. 2500 (4.58), 2830 (3.78), 2950 (3.98), 3060 (4.09), 3350 (3.68), 3510 (3.82), 4020 (3.96), 4230 (3.96).

This mixture is obviously obtained by the fission of a benzylidene group followed by ring-closure to give the two compounds shown. The formation of such a large quantity of tetracene indicates the dioxido compound (VIII) is thermally unstable. The spectrum of the mixed hydrocarbons is shown in Figure(XVIII).

-------oOo-------

E X P E R I M E N T A L.

FRIEDEL-CRAFTS REACTIONS ON PICENE.

Picene (1g) and naphthalene (5g) were finely ground together and dissolved in chlorobenzene (25ml). Aluminium chloride (20g) was added and the mixture was refluxed for 18 hours. After decomposition and removal of the chlorobenzene, the resulting yellow material was chromatographed over grade "O" alumina. Only picene (0.8g) could be isolated.

This was repeated in trichlorobenzene and tetrachloroethane and also in a naphthalene melt at 95° but no hydrocarbon was observed.

PREPARATION OF THE DILACTONE (VII).

6.11-Dichlorotetracene-5.12-quinone (5.4g) and benzyl cyanide (9g) were refluxed in ethanol (40ml) in an open vessel. Potassium hydroxide (4g) was then added over 5 minutes and the color became violet.

Dilute hydrochloric acid (10ml) was added and a dark red oil was obtained. The mixture was refluxed for a further 30 minutes and allowed to cool when a red-orange solid (6.4g) precipitated out. This compound crystallised from xylene as orange blades, m.p. 384-386° (decomp.) which gave a yellow coloration with concentrated sulphuric acid.

Found:	C, 82.9	;	H, 4.2
$C_{34}H_{18}O_4$ requires:	C, 83.1	;	H, 4.1%

DIOXIDO COMPOUND (VIII).

The above dilactone (5g) was suspended in ethanol (50ml) and potassium hydroxide (10g) in ethanol (50ml) was slowly added. The color became dark brown and a flocculent solid precipitated out. The passage of air through the boiling mixture caused a lightening in color to red, and most of the material went into solution. After refluxing for 1 hour water was slowly added to the suspension and the red-yellow solid obtained filtered off. The filtrate on treatment with sodium hydrosulphite gave a violet-red solid (22g). This crystallised from xylene as needles, m.p. 282-283°, which gave a

green going to red-brown solution with concentrated sulphuric acid.

Found: C, 88.2 ; H, 4.3

$C_{32}H_{18}O_2$ requires: C, 88.5 ; H, 4.2%

ALUMINIUM CHLORIDE MELT ON DIOXIDO COMPOUND.

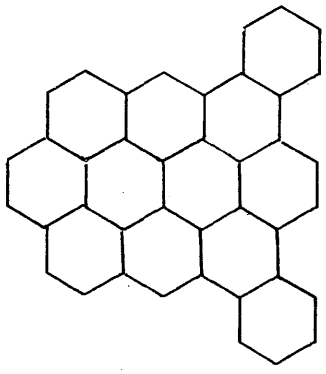
Sodium chloride (0.4g), aluminium chloride (2g) and zinc dust (0.5g) were heated to 140° and then permitted to cool to 110° when the dioxide (0.2g) was introduced. The mixture was heated at 140° for 3 minutes, the color changing from green to brown. The mixture was poured into dilute hydrochloric acid and the resulting brown resin was thoroughly washed with water and dilute ammonium hydroxide and then dried. Sublimation at 350° and 10^{-2} mm gave first tetracene (0.11g) and then a greenish-yellow solid (0.05g) which proved to be a mixture of 7.8-benzo-naphtho-[1'.3'-1.9]-anthrene (X). This crystallised from xylene as small blades, m.p. 249-250° which dissolved in concentrated acid to give a green, becoming violet solution.

Found: C, 95.1 ; H, 5.0

$C_{25}H_{16}$ requires: C, 94.9 ; H, 5.1%

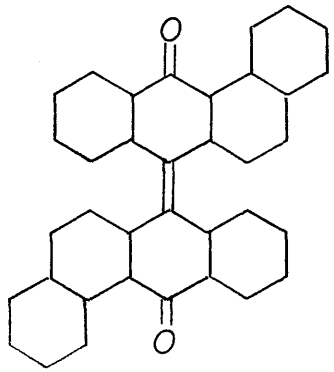
A P P E N D I X II.

PRELIMINARY INVESTIGATIONS INTO THE SYNTHESIS OF 1.2-5.6-DIBENZOVALENE.



I

INTRODUCTION: THEILACKER[1] reported the preparation of a compound which he believed to have the structure (II):



II

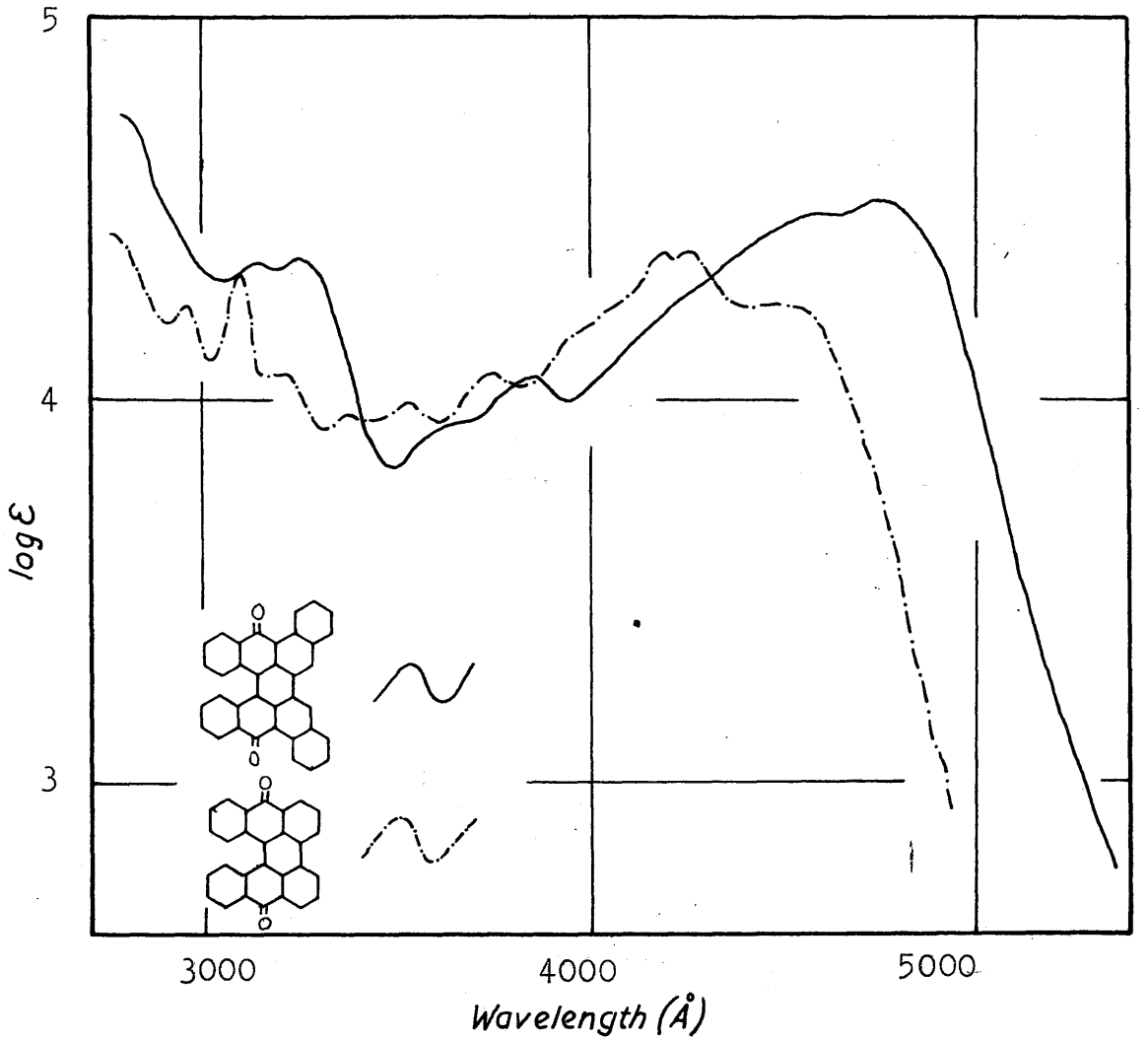
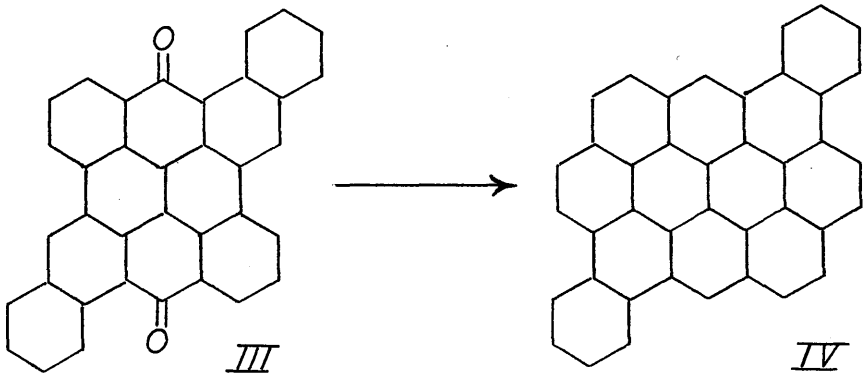


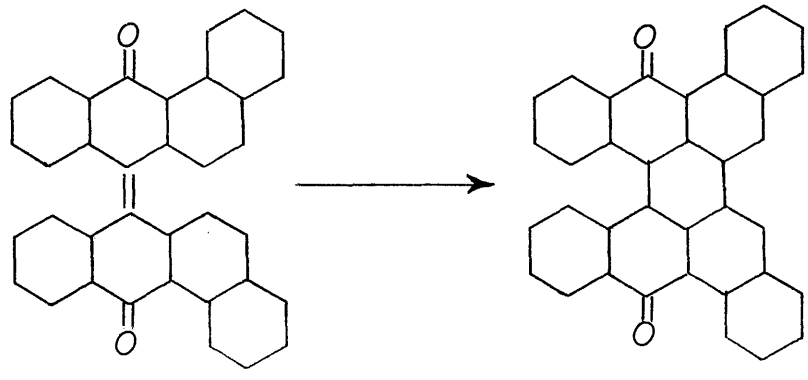
FIGURE XIX. Comparison of 2.3-5.6-7.8-10.11-Tetrabenzoperylene-3.10-quinone (VI) with helianthrone (1.2-11.12-Dibenzoperylene-3.10-quinone). Both solutions in benzene.

Accordingly it was thought that by ring-closure of this quinone, the dibenzobisanthene quinone (III) could be obtained, and from this 1.2-8.9-dibenz-ovalene (IV).



III IV

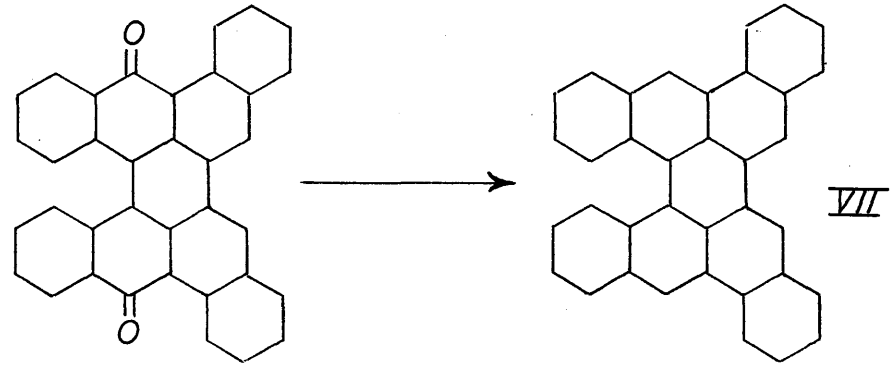
EXPERIMENTAL DISCUSSION: The quinone (II) was prepared by THEILACKER'S method[1] and was then irradiated with a quartz lamp in solution in pyridine. After some days, the pyridine was removed and dark orange needles obtained. These subsequently were shown to have the structure (VI) and hence Theilacker's quinone must have the structure:



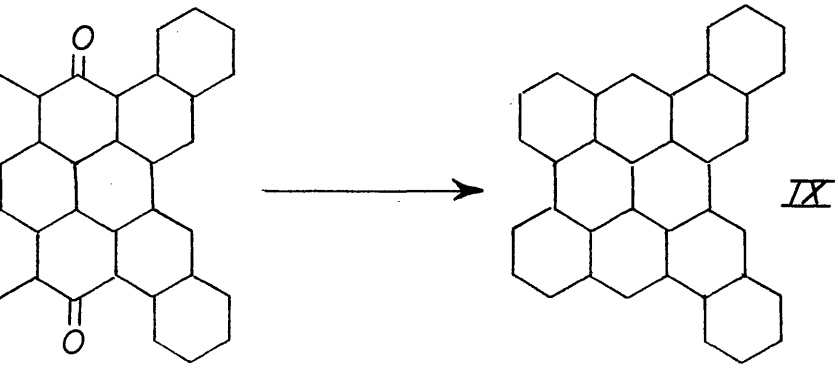
V VI

A modification was introduced into the irradiation by the addition of benzophenone as a chain-initiator This considerably reduced the time necessary for irradiation.

This quinone (VI) gave the red hydrocarbon (VII) on reduction:

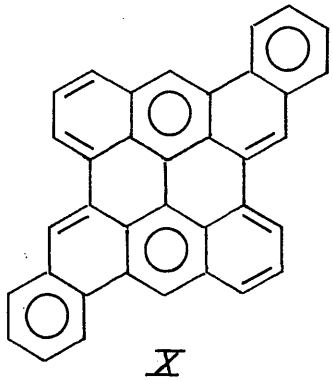
VI  VII

On treatment with aluminium chloride/sodium chloride at 160°, the dehydro-dianthrone (V) gave the dibenzobisanthene quinone (VIII) and this on reduction the blue hydrocarbon (IX).

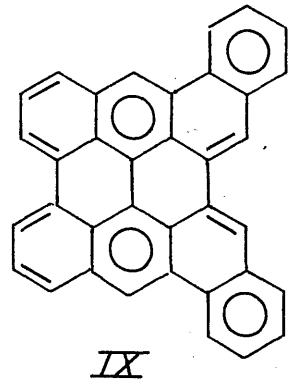
VIII  IX

It was from this latter that the proof of the structure of the dehydro-dianthrone (V) was obtained. On treatment of the blue hydrocarbon (IX) with maleic anhydride/

chloranil in xylene, a yellow anhydride was obtained. However, on further refluxing of this in maleic anhydride with chloranil, there was a perceptible lightening in color. Hence, the addition of maleic anhydride must take place in two steps. In the THEILACKER'S structure (X) the environments of the two diene units are the same and hence the structure must be as previously stated (IX):



X



IX

Lack of time prohibited any further work on this subject.

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EXPERIMENTAL.

2.3-5.6-7.8-10.11-TETRABENZOPERYLENE-4.9-QUINONE (VI).

3.4-5'.6'-Dibenzodehydrodianthrone (2g) was suspended in pyridine (40ml) and irradiated with a quartz lamp for 5 days. At the end of this time the solution was deep orange and on concentration yielded a red-brown solid which crystallised from nitrobenzene as orange needles (0.85), m.p. 362-368° (decomp.) and gave a blue coloration with concentrated sulphuric acid. These gave a green vat with sodium dithionite.

Found: C, 89.5 ; H, 4.1

$C_{36}H_{18}O_2$ requires: C, 89.6 ; H, 3.8%

This was repeated using benzophenone (0.05g) as a chain-initiator. The irradiation was then reduced to 48 hours.

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